Health risks from the exposure of children to As, Se, Pb and other heavy metals near the largest coking plant in China

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HIGHLIGHTS

- The concentration of heavy metals and metalloids in environment and children's blood are observed around the Chinese largest coking plant.
- The health risk assessments of children are analyzed.
- Foods from the coking plant are heavily contaminated by As, Cr and Se.
- Food Ingestion pathway contributes most to children's average daily dose for most heavy metals and metalloids.
- Higher potentially non-carcinogenic and carcinogenic risks happen to the local children.

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ABSTRACT

Coking influences environmental quality and poses high risks to human health as large amounts of heavy metals and metalloids are emitted into the environment from coal during the coking process. Health risks depend heavily on multi-pathway and element-specific exposures, which have, unfortunately, been rarely studied. In this study, children's health risks and exposure levels to As, Se, and heavy metals (Pb, Cd, Cr, Ni, Co, Zn, Cu, Mn, V and Sb) in the water, soil, dust, air and locally produced food were studied based on field sampling and questionnaire-based surveys around the largest coking area in China. Human blood samples were collected and analyzed to indicate the exposure levels. The non-carcinogenic risks to children mainly resulted from Cr, Mn, Pb, As and Sb, the levels of which were 3 to 10 times higher than the acceptable levels (1.0×10^{-6}). The carcinogenic risks to children were 30 to 200 times higher than the safe level (1.0×10^{-6} – 1.0×10^{-4}), which could be attributed to Cr, As and Ni pollution. The estimated risks mainly came from the pathway involving the ingestion of locally produced food, accounting for more than 85% in total for most elements. For As, the food ingestion and air inhalation exposure pathways both contributed approximately 50%, respectively. The high risks in this study highlight the attention paid to the health of children who live in the vicinity of coking activities and the importance of site-specific multi-pathway health risk assessments and food safety to protect potentially exposed children.

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1. Introduction

Coal is an important industry and the primary energy source in China, which has become the largest consumer and producer of

coal in the world (Dai et al., 2012). Coal combustion has increased dramatically during the past two decades (Ewing et al., 2010). In China, Shanxi is one of the most important province for coal production and coal-related industry (Shi et al., 2003), and much of the coal used in coal-fired power plants, coking plants and others comes from Shanxi Province (Li et al., 2012a, 2012b; Liang et al., 2010). In addition, the coking industry is a typical coal-related anthropogenic activity and important beneficial enterprise (Gorka, 2002; Wang et al., 2003). However, coal contains many types of heavy metals and metalloids, which are discharged into the environment in great amounts

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during the production process (Dai et al., 2012; Wang et al., 2010). Coal combustion and coking have been proved to be the main sources of many organic and inorganic pollutants (Dai et al., 2012; Ewing Oet al., 2010; Li et al., 2012a, 2012b; Liang et al., 2010; Wang et al., 2010).

Previous studies on coking plants or coal combustion have mainly focused on the contamination status and human health risk assessment of PAHs and on the pollution and adverse health effects of indoor air heavy metals (Moriske et al., 1996; Wang et al., 2003). However, compared with the concentration of the elements in coal from other regions, the concentrations of heavy metals and metalloids in Chinese coals, particularly Shanxi coal, are significantly higher (Dai et al., 2012). Thus, many heavy metals and metalloids in coal can be released during coking (Wang et al., 2010). Scholars have already found that coal became to be an important source of blood lead pollution in children after leaded gasoline was phased out (Liang et al., 2010). Exposure to heavy metals and metalloids, such as Pb, Cd, Ni, and As, could cause serious harm to humans (Chiodo et al., 2004; Diaz-Somoano et al., 2009; He et al., 2009; Koller et al., 2004; Zhao et al., 2012), such as lung cancer, kidney dysfunction, cognitive impairment, and chronic bronchitis neurological effects. Because of the larger absorption rate (Al-Saleh et al., 1999) and intake (Fitzgerald et al., 1998) as well as frequent hand-to-mouth activity, children are especially sensitive to heavy metal and metalloid poisoning (Fowler, 1993). Children's health-related incidents such as blood lead poisoning have attracted nationwide attention (Gao and Xia, 2011), especially in Shanxi Province with environmental pollution threatening children's health due to its plentiful coal-related industrial activities (Shi et al., 2003).

Heavy metals and metalloids could enter various environmental media, including soil, dust, drinking water, ambient air and food (Granero and Domingo, 2002; Nadal et al., 2005; Wang and Stuanes, 2003), and they may enter the human body through dermal contact, inhalation and ingestion exposure from environmental media. Previous studies have conducted human health risk evaluations of heavy metals through various exposure pathways (Baastrup et al., 2008; Hough et al., 2004; Man et al., 2010; Mari et al., 2009), but little research on the key exposure route has been performed (Qu et al., 2012), with even less focus on coking plants due to the lack of systematic multi-pathway risk analyses. Therefore, studying the contaminant levels of environmental media around coking areas and assessing the aggregated exposure to heavy metals and metalloids via various environmental media and pathways are necessary.

Human health risk assessment is widely identified as a way to estimate the nature and probability of adverse health effects in humans who may be exposed to pollutants and to present risk information to the decision maker (Qu et al., 2012). Hazard quotients (HQ), formalized by the US Environmental Protection Agency (USEPA), are widely used to characterize the non-cancer risk posed by pollutants (Granero and Domingo, 2002; Mari et al., 2009). However, risk assessment is inherently associated with uncertainty (Li et al., 2006a), which can be quantified by Monte Carlo simulation in human health risk assessment (Mari et al., 2009).

For pollutant toxicity monitoring and environmental risk assessment, biological samples such as blood are widely used as biomarker to identify the exposure levels and evaluate the environmental and occupational exposures of pollutants (He et al., 2009). We focus our study on using heavy metal and metalloid concentrations in the blood as a bio-monitoring indicator to identify the environmental and body pollution levels. The objectives of the present study are to: (1) quantify the concentration of 12 metals and metalloids in water, food, air, soil and dust around the largest coking plant in China; (2) estimate the exposure levels of metals and metalloids in children's blood; (3) quantify the exposure levels and contribution from each medium; and (4) estimate the children's health risk due to heavy metal and metalloid exposures for each medium according to the Hazard Index and cancer risk.

2. Materials and methods

2.1. Studied area

The coking plant is located in a town in the south of Shanxi Province. Coking serves as one of the most important industries in Shanxi, having been conducted for 44 years, and the province has developed a considerable and historic state-owned coking group with 4 sub-factories. According to the "Coal-Coke-Chemical" integration construction plan of the Coking Coal Group, its coking coal production capacity will reach 10 million tons per year, and its raw coal demand capacity will reach 14 million tons per year by 2015. In this studied area, besides the coking industry, there are no other enterprises and industrial activities, no highways and no busy traffic. The coal used in the coking plant was sampled in this study to detect the metal and metalloid contents in the coal and to identify the potential health risks and sources.

2.2. Sample collection and analysis

2.2.1. Human exposure survey

Based on the approval from IRB (Institution Review Board) of the National Center for Disease Control (CDC), the research on the health risk assessment of heavy metals and metalloids for children was supported by the local government and residents, and was then carried out in the selected town in Shanxi Province. A questionnaire-based survey was conducted in the studied area to determine key risk factors, such as the dietary behavior, daily activity patterns and lifestyle of the local children. Before the questionnaire-based survey and field sampling, 80 informed consent forms concerning the individual behavior pattern questionnaire and the biological samples to be collected were handed out randomly in the only primary school near the coking plant; signed informed consent forms by the participants and their guardians were ultimately obtained from 72 local participants, who were native-born and aged from 7–12 years old. The environmental samples were collected from these participants' immediate surroundings. To characterize the exposure levels of metals and metalloids in the human body, blood samples were taken from the above 72 children. For each child, 4 mL of cubital fossa venous blood was collected in vacutainers containing sodium heparin anticoagulant (Qi et al., 2002). All samples were stored at -25°C until analysis.

2.2.2. Field sampling

In the studied area, the drinking water is tap water, which is provided by an ancient spring. A total of 13 samples were collected in 1 L acid-washed polyethylene bottles from local families at random to represent the whole area, and 2 samples were collected from the school to avoid the differences in environment and use of pipe. After adding two drops of 65% concentrated HNO_3 into the water, they were stored at -20°C until analysis.

Soil samples (1 kg) were collected from the upper soil layer (0–20 cm) at 13 sites, including abandoned residential areas and crop fields. In each sampling site, the soil samples were integrated randomly with 4–5 equal portions in an area of 100 cm^2 (Zhang et al., 2010), which were selected from undisturbed points. To study the impact of the deposition of coal combustion fly ash on the ground, dust samples (5 g) were collected from the street at the coking plant. As the selected children spent almost half the day at both school and home and the residences were mainly commercial buildings, another four dust samples were collected from the roads outside the residential buildings and the classroom and stairs of the school. Each sample was mixed with 4–5 random sub-samples.

Seventeen common fresh vegetable species (2 kg) were collected from farmer's markets for this study: chrysanthemum, white radish, pumpkin, zucchini, chive, parsley, potato, lettuce, garlic bolt, asparagus lettuce, cayenne pepper, Chinese cabbage, kidney bean, cucumber,

spinach, bok choy cabbage, tomato and eggplant. Since wheat is the staple food, then nine wheat samples (2 kg) produced from the town were also collected for element analysis. Each species was integrated with 3–5 sub-samples.

Fine particulate matter (PM_{2.5}) from 3 representative monitoring sites, namely the primary school, residential district and coking area, were collected simultaneously using a low-volume breathing sampler (Buck Libra Plus, AP BUCK Inc., U.K) with a flow rate of 2 L min⁻¹ for 12 h. Indoor and outdoor samples were collected at the same time. Before and after sampling, all quartz microfiber filters were pretreated by previously established methods (Hu et al., 2012).

2.2.3. Sample treatment

Water samples were filtered using Whatman No.1 filter paper and stored at 0–4 °C. After thoroughly thawing and shaking, whole blood samples (1 mL) were digested using microwave digestion in acid-clean Teflon vessels with a preparation system (Liu et al., 2009). During the pre-treatment of aerosol samples, the entire piece of filter paper was digested for the element analysis (Hu et al., 2012). After air-drying and removal of the shell fragments, the soil and dust samples were ground with an agate mortar and sieved with a nylon membrane sieve (0.071 mm) to obtain a fine homogenous powder. Then, a sample of fine powder (0.1000 g) was weighed for digestion (Zhang et al., 2010). The edible parts of the food samples (vegetable and wheat) were cut into small pieces after thoroughly washing with tap water and deionized water. After freeze-drying, the foods (0.5000 g) were ground and sieved for analysis before acid digestion (Li et al., 2006b). For quality control, each digestion batch included a reagent blank, a representative reference standard and typically an analytical blank and duplicate to assess the performance of process and efficacy and to validate the established method. Spiked recovery was conducted for the aerosol samples due to the lack of reference materials. The recoveries of the elements ranged from 85% to 117%. All the chemical reagents in the experiments were guaranteed reagents.

2.2.4. Sample test

After pre-preparation, all digested and made-up sample solutions were filtered and diluted to the appropriate concentration. The concentrations of Cu, Zn, Co, Cr, Cd, Pb, Ni, Sb, As, Se, Mn and V in all samples were measured by ICP-MS (Agilent-7500a, Agilent Scientific Technology Ltd., USA) under the optimized conditions (Zhang et al., 2010). The results were quantified using an empirical calibration curve generated from the responses obtained from multiple dilutions of a multi-element calibrations standard (Agilent Scientific Technology Ltd., USA).

2.3. Exposure assessment via ingestion, dermal contact and inhalation

According to the Exposure Factors Handbook (USEPA, 1997), the average daily dose (ADD) (mg kg⁻¹ day⁻¹) of an element via the ingestion, inhalation and dermal contact exposure pathways can be estimated using Eqs. (1), (2), and (3), respectively:

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

$$ADD_{\text{inhale}} = \frac{C \times t \times \text{InhR} \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{BW} \times \text{AT}} \quad (2)$$

$$ADD_{\text{dermal}} = \frac{C \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{ED} \times \text{EF}}{\text{BW} \times \text{AT}} \quad (3)$$

where C is the concentration of the element in mg kg⁻¹, IngR is the ingestion rate in mg day⁻¹, InhR is the inhalation rate in m³ day⁻¹, t is the exposure time in h day⁻¹, PEF is the inhalation factor for the respirable particles in m³ kg⁻¹, SA is the surface area of the skin exposed to pollutants in cm², AF is the skin adherence factor in mg (cm² h)⁻¹, ABS is the dermal absorption factor, EF is the exposure frequency in

days year⁻¹, ED is the exposure duration in year, BW is the body weight in kg, AT is the average time in days.

To calculate the ADD of each pathway, the ingestion rate of drinking water and food and the children's body weight were obtained through the questionnaire-based exposure survey. The other exposure parameters, such as the IngRs of the soil and dust and SA, were obtained from the literatures (Duan, 2012; Duan et al., 2011; USEPA, 1997, 2002; Zheng et al., 2010) and are listed in Table S1 (supplementary data). The penetration coefficient factor for water exposed in humans by dermal contact is listed in Table S2.

2.4. Risk calculation

Based on the ADDs from the 3 exposure routes, a Hazard Quotient (HQ) indicating the non-cancer risk during a lifetime can be calculated by dividing the ADD from each exposure route by a specific reference dose (RfD) or by a reference concentration in air (RfC). The HQ is defined as follows (USEPA, 2011a):

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

where RfD is the estimated maximum permissible risk on humans through daily exposure. There are three thresholds: RfDo (mg kg⁻¹ day⁻¹) for ingestion, RfDd (mg kg⁻¹ day⁻¹) for dermal contact and RfCi (mg m⁻³) for inhalation. Experiencing adverse health effects is unlikely when HQ ≤ 1, whereas there may be concern for potential non-carcinogenic effects when HQ > 1 (Al-Saleh et al., 1999).

Moreover, to assess the overall potential non-carcinogenic effects posed by more than one chemical (e.g., i), the HQ calculated for each chemical is summed (assuming additive effects) and expressed as a Hazard Index (HI) (USEPA, 1986):

$$HI = \sum_1^i HQ \quad (5)$$

If there are multiple pathways, a total exposure Hazard Index (HIt) could be used to communicate the non-cancer risks through different pathways, which is expressed as follows (USEPA, 2011a):

$$HIt = \sum_1^i HI(\text{Exposure pathway}_1) \quad (6)$$

In the case of HIt ≤ 1, the assumption is that no chronic risks are likely to occur. In contrast, for HIt > 1, non-cancer risks are likely to occur, and thus segregating the contaminants and separating HIt for the analysis would be appropriate.

For the cancer effect, the Incremental Lifetime Cancer Risk (ILCR) is estimated as the incremental probability of an individual developing cancer over a lifetime due to exposure to a potential carcinogen. The ILCR is defined as follows (USEPA, 2011a):

$$ILCR = ADD \times \text{SF} \quad (7)$$

The SF (cancer slope factor) is listed in Table S2. If there are multiple carcinogenic contaminants, the cancer risk for each carcinogen and exposure route are added (assuming additive effects) and compared with the acceptable risk. Risks in the range of 1.0 × 10⁻⁶ to 1.0 × 10⁻⁴ have been judged to be acceptable.

According to the classification group orders defined by the IARC (International Agency for Research on Cancer) (IRAC, 2011), Pb, Zn, Cu, Mn, Cr, Cd, et al., were regarded as non-cancer effect elements, while Cr, Cd, As, Ni and Co were treated as having potential carcinogen effect. The SF, RfD, RfC, GIABS (gastrointestinal absorption factor used for calculating dermal SF) et al., are listed in Table S2 (USEPA, 2011b).

Table 1
Concentration of heavy metals and metalloids in environmental media.

Contaminant	Value	Pb	Cr	Mn	Co	Ni	Cu	Zn	Cd	V	As	Se	Sb
Soil	Median	22.14	27.51	601.58	12.10	30.78	71.93	63.47	0.27	72.79	21.49	70.52	11.33
	Mean	24.10	81.51	593.06	12.00	31.42	73.55	69.41	0.30	71.15	51.51	66.69	11.33
Dust	Median	29.24	172.28	625.32	8.82	24.26	37.26	127.99	0.45	57.22	10.92	0.29	0.85
	Mean	37.88	188.88	602.44	8.85	23.87	60.16	178.86	0.61	53.26	10.67	0.59	0.94
Ambient air	Median	0.24	20.69	0.33	0.02	0.32	1.02	1.28	0.11	0.04	7.01	0.17	0.11
	Mean	0.26	17.69	0.34	0.03	0.29	1.14	1.27	0.11	0.06	6.63	0.20	0.10
Drinking water	Median	0.72	6.79	1.40	0.13	1.36	0.69	98.82	0.04	2.14	0.08	0.51	0.92
	Mean	1.36	6.52	2.05	0.14	1.41	2.15	180.12	0.04	2.65	0.10	0.55	0.94
Vegetable	Median	0.18	1.35	31.96	0.07	1.16	6.50	30.69	0.06	0.20	1.58	0.39	0.09
	Mean	0.26	2.11	32.22	0.11	1.28	7.26	37.12	0.13	0.35	1.91	0.53	0.10
Staple food	Median	0.29	5.45	32.87	0.04	2.32	4.08	29.83	0.02	0.09	0.06	0.10	0.02
	Mean	0.40	9.39	60.31	0.22	2.58	5.88	36.21	0.04	0.48	4.88	1.14	0.21

2.5. Statistical analysis

To accommodate the uncertainties associated with the calculation process and exposure factors, Monte Carlo simulations were applied with Crystal ball software (16.0), and 10,000 iterations were calculated. The statistical analysis and multiple regression analysis were performed by SPSS (20.0) software.

3. Results and discussion

3.1. Contents of heavy metals and metalloids in environmental media

The contents of the heavy metals and metalloids in the environmental media are listed in Table 1. As shown, except for As contamination in the soil, the mean values of Cu, Ni, Pb, and other metal(loid)s in the soil and dust were in accordance with the natural background levels in the soils of Shanxi (Fitzgerald et al., 1998; Shi et al., 1994). This could have resulted from the observations that the pollution source in the area is the sole coking plant and that the concentrations of these heavy metals and metalloids in coal are low (Dai et al., 2012).

The tap water in the studied area is considered safe as all the heavy metal and metalloid concentrations were less than the national drinking water quality standard. This outcome mainly occurred because the concentrations of metal(loid)s in the water source are low and the pilot process is quite short, which reduces the potential for pollution during transportation. However, the mean concentrations of Cr, As, Se and Zn in vegetables were 4.2, 38.2, 5.3 and 1.5 times higher, respectively, than the limited values defined in the standards. In comparison, the mean contents of Cr, As, Se and Zn in wheat were 5.8, 10.3, 0.93 and 1.49 times higher, respectively, than the thresholds. The results, indicating that foods were contaminated by Cr, As, Se and Zn, were in accordance with the findings of a previous study (Zeng et al., 2007) and confirmed the outcome that although the contents of metal(loid)s in the soil were not high, Cr, As, and Zn could accumulate in vegetables, leading to contamination (Ma et al., 2006). In addition, the bivariate correlation of the Pb and As contents in vegetables was found (Spearman $r = 0.713$, $p < 0.05$), and the correlation of both As and Se in the vegetables and wheat was significant (Spearman $r = 0.951$, $p < 0.01$; Spearman $r = 0.996$, $p < 0.01$, respectively). The results revealed the same pollution source may be responsible for the Pb, As and Se in food. Furthermore, to study the pollutant status of each species, the concentrations of heavy metals and metalloids of all species were listed in Table S3. Compared with the Chinese lead thresholds in food which are defined based on

different vegetable, only six kinds of vegetables exceeded the threshold for lead contents. And various vegetables showed different adsorption properties of heavy metals in the soil, as previous studies found that the occurrence of heavy metal accumulation of leafy vegetables was highest, followed by stem vegetables, while that of fruit vegetables was lowest, and the accumulation of heavy metals for different types of vegetables showed a significant positive correlation with the contents of heavy metals in soil (Xu et al., 2008). However, some scholars have found that there is no correlation between the contents of heavy metals in soil and in vegetables (Liu et al., 2006). In this study, leafy vegetables (cabbage, spinach, lettuce, parsley, etc.) accumulated much higher amounts of Pb compared to stem vegetables (white radish and garlic) and fruit vegetables (pumpkin, cucumber, capsicum, eggplant and green beans). But, there is no significant correlation between the contents of heavy metals in soil and in vegetables. The variance in the accumulation of heavy metals in each vegetable may be attributed to the difference in effectiveness of various soil properties and to the difference in sensitivity of various vegetables.

For fine particulate matter (PM_{2.5}), the results showed that Cr, Zn, Cu and As were the most abundant pollutants, which was similar to those of a previous study (Hu et al., 2012). The observation that the coal used in the coking plant has higher concentrations of metal(loid)s compared with those of coals from other regions could be the key reason (Table S4). However, the contents of As, Pb, and other metal(loid)s in PM_{2.5} were relatively lower in our studied area compared with other counterpart areas (Widory et al., 2004; Chen et al., 2005; Li, 2005). This finding may be because of the single industrial emission source and low level contents of metal(loid)s in coal compared with ore and other sources (Chen et al., 2005; Dai et al., 2012). In this study, Zn and Cr in PM_{2.5} showed a strong significant correlation with Se in PM_{2.5} (Spearman $r = 0.857$, $p < 0.05$; Spearman $r = 0.864$, $p < 0.05$, respectively). Coal combustion has been described as the main contributor of As and Se in the ambient environment (Li, 2005) and therefore, Cr, Zn, Cu and As in PM_{2.5} may be the result of coal combustion.

In addition, the concentrations of Co and Ni in wheat showed a strong significant correlation with those in ambient air (Spearman $r = 0.910$, $p < 0.05$; Spearman $r = 0.890$, $p < 0.05$, respectively), while the concentration of Co in drinking water showed a strong significant correlation with that in dust (Spearman $r = 0.905$, $p < 0.05$). This may indicate that the Co and Ni pollution in ambient air may be an important pollution source for Co and Ni pollution of wheat, since the pollutants in air could be important pollution sources for plants. And for drinking water, the concentration of Co presented a significant correlation with that in dust. Though the drinking water in the town

Table 2
Concentration of heavy metals and metalloids in children's blood.

Content	Value	Pb	Cr	Mn	Co	Ni	Cu	Zn	Cd	V	As	Se	Sb
Blood	Median	3.85	10.16	1.86	1.12	5.09	44.47	30.41	7.16	1.41	0.95	2.92	5.08
	Mean	5.24	11.84	2.17	1.43	6.69	53.51	34.42	8.51	1.68	1.08	5.27	5.03

Fig. 1. The contribution of ambient air, water, soil, dust and food via inhalation, ingestion and dermal contact to the average daily exposure dose.

is safe for consumption, it may be contaminated and may have the same pollution source as that of dust.

3.2. Contents of heavy metals and metalloids in children's blood

The concentrations of heavy metals and metalloids in the blood were shown in Table 2. Cr, Cu, Zn were the most abundant elements in blood. Pb showed a significant correlation with Cu, Mn and Sb, implying that Pb, Cu, Mn and Sb may have had the same pollution source. However, similar to a previous study, a negative correlation was found between Pb and Zn, which may be associated with the observation that zinc plays an important role in lead metabolism (Wang and Stuanes, 2003). There were also significant correlations among Cr, Mn, Co, Ni and Cd, implying that Cr, Mn, Co, Ni and Cd may have the same pollution source.

Blood lead level (BLL) is widely used as a biomarker to evaluate the exposure to Pb in the general population. According to the new updated criteria defined by the US Centers for Disease Control (http://www.cdc.gov/nech/lead/ACCLPP/blood_lead_levels.htm), children with a BLL $\geq 5.00 \mu\text{g dL}^{-1}$ were considered to have an elevated BLL. The Pb level in the children's blood was $5.25 \pm 3.85 \mu\text{g dL}^{-1}$, which was slightly higher than the updated criteria, and the prevalence rate of elevated BLLs was 8.3% in this study. However, the prevalence rate was lower

than that at the national level, which was a BLL of $8.07 \mu\text{g dL}^{-1}$ (23.9%) (He et al., 2009). This variance can be explained by the observation that both the highest BLLs and prevalence rate occurred in children aged 5–6 years (He et al., 2009); however, the population studied herein was mainly aged from 7 to 12 year, a group in which the children may perform fewer hand-to-mouth activities (Wu et al., 2011). Moreover, the heaviest lead-contaminated zone in the air was 75–100 cm over ground (Dong et al., 2001), which is the height range for normal Chinese children of 5–6 years (Wang and Zhang, 2006; Zhang, 2007). In this study, the height of the children ranged from 120 to 164 cm, which was higher than the heaviest lead-contaminated zone. In addition, the children's BLLs in this study were lower than that of children living around a copper-smelter (Carrizales et al., 2006) and around an E-waste recycling industrial area (Zheng et al., 2008). Except for the age factor, the coking industry produced much lower Pb emissions due to a lower Pb content in coal than that in ores and E-waste (Hilts, 2003; Zheng et al., 2008).

Moreover, among the heavy metals and metalloids, the Pb concentration in children's blood did show a significant negative correlation with that in dust (Spearman $r = -0.900$, $p < 0.05$), while the As concentration in children's blood showed a significant positive correlation with that in dust (Spearman $r = 0.875$, $p < 0.05$). This illustrates that Pb in dust was not an important pollution source for children's

Table 3

Summary of non-carcinogenic and carcinogenic risks via dermal contact, ingestion and inhalation exposure of soil, dust, drinking water, food and ambient air on children (7–12) based on the total element concentrations and field measurements of the exposure factors at the 5th, median and 95th percentiles.

Metal(loid)s	5%				Median				95%			
	HI _{ing}	HI _{inh}	HI _{dermal}	HI _{lt}	HI _{ing}	HI _{inh}	HI _{dermal}	HI _{lt}	HI _{ing}	HI _{inh}	HI _{dermal}	HI _{lt}
Non carcinogenic effects (HI)												
Pb	1.01E+00	4.84E-03	2.50E-05	1.02E+00	2.36E+00	6.72E-03	4.90E-05	2.36E+00	4.06E+00	8.78E-03	6.51E-05	4.06E+00
V	1.04E-01	2.86E-01	1.01E-05	3.99E-01	2.81E-01	3.97E-01	1.92E-05	6.83E-01	5.61E-01	5.21E-01	2.65E-05	1.08E+00
Cr	7.26E-01	2.15E+00	3.31E-03	2.92E+00	1.55E+00	2.18E+00	5.91E-03	3.73E+00	2.28E+00	2.22E+00	8.05E-03	4.50E+00
Mn	4.50E-01	1.22E+00	3.79E-05	1.75E+00	1.15E+00	1.70E+00	7.00E-05	2.84E+00	1.99E+00	2.24E+00	9.71E-05	4.01E+00
Co	6.01E-02	1.02E-01	2.65E-03	1.79E-01	1.79E-01	1.42E-01	5.13E-03	3.30E-01	3.73E-01	1.86E-01	7.17E-03	5.11E-01
Ni	4.70E-01	2.64E-03	5.29E-05	4.73E-01	1.06E+00	3.65E-03	9.49E-05	1.06E+00	1.62E+00	4.78E-03	1.31E-04	1.62E+00
Cu	5.14E-01	4.71E-03	3.84E-06	5.19E-01	1.39E+00	6.53E-03	7.72E-06	1.40E+00	2.61E+00	8.55E-03	1.06E-05	2.62E+00
Zn	3.15E-01	4.96E-04	7.01E-07	3.16E-01	7.49E-01	6.83E-04	1.36E-06	7.49E-01	1.29E+00	8.94E-04	1.88E-06	1.29E+00
As	2.32E+00	3.35E+00	3.45E-04	5.71E+00	5.63E+00	4.63E+00	7.01E-04	1.03E+01	8.63E+00	6.06E+00	9.56E-04	1.48E+01
Se	3.55E-01	5.32E-01	2.05E-05	8.94E-01	8.89E-01	7.37E-01	4.21E-05	1.65E+00	1.41E+00	9.65E-01	5.80E-05	2.38E+00
Cd	2.50E-01	4.29E-01	9.46E-06	7.44E-01	7.64E-01	5.98E-01	1.79E-05	1.36E+00	1.57E+00	7.80E-01	2.44E-05	2.14E+00
Sb	1.52E+00	1.95E-01	1.39E-04	1.72E+00	3.41E+00	1.95E-01	2.78E-04	3.61E+00	5.55E+00	1.95E-01	3.80E-04	5.75E+00
Total	8.09E+00	8.28E+00	6.60E-03	1.66E+01	1.94E+01	1.06E+01	1.23E-02	2.88E+01	3.19E+01	1.32E+01	1.70E-02	4.47E+01

blood lead levels, but As pollution in dust may be responsible for the As in children's blood.

3.3. Daily exposure dose of heavy metals and metalloids

The human exposure to heavy metals and metalloids mainly occurs through the routes of inhaled aerosol particles, dusts, soil, food, and drinking water (USEPA, 1997), whereas the main pathways for children include aerosol inhalation, hand-to-mouth activities, and dermal contact (Diaz-Somoano et al., 2009). Based on the contents of heavy metal(loid)s in each environmental medium and the intake rates of ambient air, drinking water, food and soil/dust of children obtained from the questionnaires, the daily exposure doses of heavy metals and metalloids of children were evaluated. The contribution of each exposure route to children's average daily dose (ADD) is shown in Fig. 1.

According to the results, food ingestion played an important role in the total ADD of children for most metal(loid)s, especially for Cu, Ni and Mn, which accounted for 99.13%, 99.01% and 98.86%, respectively. However, for As, the inhalation pathway through ambient air (46.53%) contributed nearly as much as the ingestion pathway through food (52.07%). In addition, the daily intake of metal(loid)s via ingestion of staple foods and vegetables were 1.6124 and 1.6053 mg (kg d)⁻¹, respectively. The intakes of Cr, Ni, As and Se in staple foods accounted for the majority of the total ADD, implying that staple foods could pose a higher risk to the local children via the ingestion pathway. For the inhalation pathway, the exposure dose of most metal(loid)s from the interior accounted for more than 90% of the total exposure dose. Furthermore, for indoor air exposure, the dose of school exposure was less than that of home, which would be associated with either higher pollution at home, or a relatively longer time spent at home (based on the questionnaires).

3.4. Risk characteristics

3.4.1. Non-cancer risk

Based on the ADD and RfD of each pollutant, the non-cancer risks of heavy metal(loid)s to the local children were calculated. As the HQs do not always exhibit a normal distribution after a normality test using the Kolmogorov–Smirnov's method, the HI and HIt of the ingestion, dermal contact and inhalation pathways are shown for the 5th, median and 95th percentile (Table 3). The HIt of heavy metals and metalloids in children decreased in the order of As > Cr > Sb > Mn > Pb > Se > Cu > Cd > Ni > Zn > V > Co, showing that As was potentially highly deleterious to health. As mentioned previously, As and Se in the ambient environment were mainly attributed to coal combustion. Therefore, considering that the coking plant is the sole potential pollution source, As and Cr, et al., in the study area, posing heavy health risks to local

Fig. 3. Multi-pathway analysis of HQ (As). Each pathway's contribution to the total As exposure of the local children.

children, would be caused by coal combustion during the coking process in the coking plant. However, further research is needed to identify the extent to which the coking plant increased the risks of exposure to heavy metals and metalloids.

Table 3 indicates that ingestion appeared to be the main pathway for Pb, Cr, Mn, Ni, Cu, As and Sb exposure, followed by inhalation exposure. As, Cr and Mn would be the main contributors to the children's exposure to pollutants through inhalation exposure. Therefore, dermal contact via water, suspended particles of soil and dust routes was almost negligible. The HIs for metal(loid)s in children from ingestion exposure decreased in the order of As > Sb > Pb > Cr > Cu > Mn > Ni > Se > Cd > Zn > V > Co. Compared with the order of HIt for metal(loid)s, Pb, Cu and Ni showed an accelerated trend and illustrated that the ingestion exposure of these heavy metals contributed greatly to the non-cancer effect. Dividing the ingestion exposures into different routes, Table S5 illustrates that the ingestion exposure of food contributed greatly to the HQ for all metal(loid)s. The HQ of As via food ingestion exceeded 1 even at the 5th percentile. Combined with Fig. 1 and the food ADD, the ingestion exposure of staple foods was the most likely route for children, posing a risk to the children living in the coking area. This means that the pollutants in staple foods would be the main and direct pollution source for the children's exposure to heavy metal(loid)s. For most metal(loid)s, the HQs via the soil route were slightly higher than those via the dust route as the IngR of the soil was higher than that of dust. Table S6 shows that the inhalation pathway of ambient air was the predominant exposure source. In particular for Cr, Mn and As, the HQs via ambient air inhalation were 1.0×10^3 to 1.0×10^6 times higher than those of the soil and dust inhalation exposure routes. The

Fig. 2. Multi-pathway analysis of HQ (Pb). Each pathway's contribution to the total Pb exposure of the local children.

Fig. 4. Multi-pathway analysis of HQ (Cr). Each pathway's contribution to the total Cr exposure of the local children.

Fig. 5. Cumulative probability distribution of the HQ of As from food ingestion. The health risk was evaluated by means of a Monte Carlo simulation based on Crystal ball soft for 10000 iterations.

HQs of Cr, Mn and As were all higher than 1, indicating that the high content of Cr, Mn, and especially As in the ambient air would pose a harmful effect to the local children.

The results illustrated that for the potential non-carcinogenic risk, the combined HI for all heavy metals and metalloids was 16.6, 28.8 and 44.7 at the 5th, median and 95th percentiles. Compared with previous results (Qu et al., 2012), except for the site-specific contaminants and lifestyle, the higher non-carcinogenic risks in this study could also be explained by the fact that more toxic metal(loid)s in the integrated exposure pathway were taken into consideration for the health effect in this study. Furthermore, based on the questionnaire-survey on the dietary and behavior patterns, the children preferred local food, which has relative higher contents of heavy metals and metalloids. Cr, Mn and As were the main contributors through the inhalation pathway. The ingestion exposure for Pb, As and Sb was an important pathway and may be detrimental to children even at the 5th percentile. The HI of Pb, Cr, Mn, Ni, Cu, As and Sb via the ingestion pathway exceeded 1 at the 50th percentile. However, the HI value for all heavy metals and metalloids through dermal contact was less than 1, even at the 95th percentile. These results indicated that, although the surrounding environments were not heavily polluted by heavy metal(oid)s and the children were not exposed to a heavily polluted environment, the heavy metal(oid)s in the environmental media may pose high health risks to the local children by several exposure pathways due to the certain intake from each exposure media. The majority of the non-cancer risks were contributed by Cr, Mn, Cu, Pb, Ni, As, and Sb from ingestion and inhalation exposure, while the adverse health effects on children through dermal contact could be ignored. Using As, Cr and Pb as examples, each pathway's contribution to the total exposure of the local children was calculated based on the average HQ values, as shown in Figs. 2–4.

As shown in Fig. 2, the exposure to this non-essential element was mainly from food ingestion, which contributed 97.32% to the total Pb HQ. The vegetables and wheat contributed nearly equally. Inhalation exposure and dermal contact contributed little. Compared with a previous study

(Qu et al., 2012), the results found that the contribution of different exposure pathways was similar to the village in the previous study which was closest to the mine area. The local children's exposure to As mainly occurred through staple food ingestion and indoor air inhalation exposure, and home indoor air contributed more than school indoor air (Fig. 3). Air inhalation was the primary pathway to Cr exposure (Fig. 4), which contributed nearly three-fifths to the total HQ. The Indoor air exposure pathway was the most important for Cd air inhalation exposure, accounting for 94.56%. However, home indoor air contributed 3.5 times as much as did school indoor air. Food consumption contributed two-fifths to the total HQ, and among the different types, wheat was highly significant, contributing 65.08%. To accommodate the uncertainties associated with the calculation process and exposure factors, the HQ of As from food ingestion was taken as an example to evaluate the calculation using a Monte Carlo simulation, as shown in Fig. 5. The median value of HQ was 5.28, which was close to the calculated value of 5.27 (Table S5), indicating that there was likely no bias in the risk evaluation in this study and that higher potential risks were posed to the local children.

3.4.2. Cancer risk

Table 4 shows that there was no cancer risk from the pollutants to children through the dermal contact pathway. However, the results illustrated that the carcinogenic risk through the ingestion exposure pathway was mainly attributed to Cr and Ni, which had carcinogenic risk levels that were 10 and even 100 times higher than the acceptable level ($<1.0 \times 10^{-4}$). In addition, As could pose potential carcinogenic risks to children, with its risk levels being higher than the acceptable level. Taking the ADD and contents of metal(loid)s into consideration, the study that Cr, Ni and As exposure from staple foods would pose a potential higher carcinogenic risk to the local children.

Moreover, the carcinogenic risks posed by Co, Ni and Cd inhalation exposure were lower than 1.0×10^{-4} and could be considered acceptable. The carcinogenic risk from Cr inhalation exposure was slightly higher than 1.0×10^{-4} and would not be negligible. However, the potential high carcinogenic risk via inhalation exposure pathway was

Table 4

Summary of carcinogenic risks (ILCR) via dermal contact, ingestion and inhalation exposure of soil, dust, drinking water, food and ambient air on children (7–12) based on the total element concentrations and field measurements of the exposure factors at the 5th, median and 95th percentiles.

Metal (loid)s	5%				Median				95%			
	Ingestion	Inhalation	Dermal	Sum	Ingestion	Inhalation	Dermal	Sum	Ingestion	Inhalation	Dermal	Sum
Cr	1.33E-02	2.68E-04	1.05E-06	$\Sigma = 1.35E-02$	2.74E-02	3.84E-04	2.10E-06	$\Sigma = 2.78E-02$	4.52E-02	4.90E-04	2.57E-06	$\Sigma = 4.56E-02$
Co	NA	3.80E-06	NA	$\Sigma = 3.80E-06$	NA	5.40E-06	NA	$\Sigma = 5.40E-06$	NA	6.80E-06	NA	$\Sigma = 6.80E-06$
Ni	2.24E-03	6.10E-06	2.62E-07	$\Sigma = 2.20E-03$	4.91E-03	8.80E-06	5.23E-07	$\Sigma = 4.92E-03$	8.58E-03	1.11E-05	6.37E-07	$\Sigma = 8.59E-03$
As	1.64E-04	2.04E-03	2.25E-08	$\Sigma = 2.28E-03$	3.57E-04	2.91E-03	4.48E-08	$\Sigma = 3.27E-03$	6.21E-04	3.66E-03	5.43E-08	$\Sigma = 4.20E-03$
Cd	NA	2.07E-05	NA	$\Sigma = 2.07E-05$	NA	2.97E-05	NA	$\Sigma = 2.97E-05$	NA	3.75E-05	NA	$\Sigma = 3.75E-05$
Total	1.57E-02	2.34E-03	1.33E-06	$\Sigma = 1.80E-02$	3.27E-02	3.34E-03	2.67E-06	$\Sigma = 3.68E-02$	5.44E-02	4.21E-03	3.26E-06	$\Sigma = 5.84E-02$

NA—not applicable.

mainly caused by As inhalation, accounting for nearly 87%. The exposure dose of As was considered to be detrimental to children via ingestion, inhalation and dermal contact (USEPA, 2011b). Thus, results in this study showed high carcinogenic risk levels ($>1.0 \times 10^{-4}$), which were in accordance with the results of a previous study due to the high As pollution in the studied area (Li, 2005).

3.5. Uncertainty analysis

Ideally, the contaminant status of heavy metals and metalloids in the body and environment should be illustrated by a certain number of samples and better illustrated by a follow-up investigation. However, only a few biological samples and environmental samples were analyzed because of the limitations of people's cooperation during the sampling process.

Using bioavailable or bioaccessible elements concentrations (Brown et al., 1999) to conduct human non-carcinogenic and carcinogenic risk evaluations is considered to be the most reliable and accurate method (Oomen et al., 2002). However, animal experiments to quantify the bioavailable element concentrations and estimate the human health risk usually are costly and could suffer from ethical concerns, whereas in vitro digestion models are not suitable for estimating both the dermal contact and inhalation exposure. In this study, the total elements concentrations were used to estimate the carcinogenic and non-carcinogenic risks in children. Thus, the health risk assessments in this study could be somewhat overestimated. Although these risk assessments may not provide an absolutely accurate picture of the risk level, this study provided the preliminary implementation of a well-defined investigation of the coking area on the health risk assessment of heavy metals and metalloids. The extent to which the coking plant poses health risks to the local children, because of exposure to heavy metals and metalloids, was not researched in this study due to the limitations of the questionnaire and field research. However, it encourages further research using other methods to identify the contribution of the coking plant to the local children's health risks.

4. Conclusion

There was heavy contamination of As, Se and Cr in the food. Ingestion via food was the main exposure pathway in children exposed to heavy metals and metalloids. The Cr, Ni and Cd et al., in children's bodies may have the same pollution source. Except for As pollution in food, As pollution in dust was also responsible for the As content in children's blood. Based on the concentration of pollutants, the RfD, exposure factors, and other factors, the non-carcinogenic risks to children mainly resulted from Cr, Mn and As via inhalation exposure and from Pb, Cr, Mn, Ni, Cu, As and Sb via ingestion exposure. The integrated carcinogenic risks to the children mainly resulted from Cr, As and Ni via ingestion exposure and As via inhalation exposure. Both the cancer and non-cancer risks through dermal contact could be ignored. Therefore, attention should be paid to the health risks due to the children's exposure to As and other heavy metals in the region near the largest coking plant in China, given the present quality standards.

In addition, to provide a fuller picture to estimate the human health risk of pollutants, the further investigation of bioaccessible elements is highly recommended. And, the contributions of the pollutants from the coal combustion in the coking plant to the children's internal exposure encourages in-depth research in the future.

Conflict of interest

This work was supported by the Special Environmental Research Funds for Public Welfare (No. 201109064 and No. 201009046). The views expressed in this manuscript are solely of the authors and do not necessarily reflect those of the funding agencies. The biological samples were collected after the informed consents forms were written

and handed in by the participants, and there's no conflict of interest between the participants and researchers in the whole study.

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, "Health risks from the exposure of children to As, Se, Pb and other heavy metals near the largest coking plant in China."

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.11.124>.

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