Risk assessment of atmospheric heavy metals exposure in Baotou, a typical industrial city in northern China

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Abstract Industrial activities have led to serious air pollution and the potentially toxic elements in atmospheric particles can cause various health problems to humans. In this study, inhalable particulate matter (PM$_{10}$) and fine particles (PM$_{2.5}$) were collected from four typical sites in Baotou, an industrial city in northern China. We investigated both the mass concentrations of particulate matter and the concentrations of heavy metals (Cr, Ni, Pb, Cd, Cu, Mn, Co, and Zn) in the collected samples. We assessed the public health risks associated with atmospheric heavy metal exposure. The results showed that the mass concentrations of PM$_{2.5}$ and PM$_{10}$ as well as these heavy metal concentrations varied notably influenced by the prevailing wind directions. Among the studied metals, Zn, Mn, Pb, and Cr were the main metal pollutants in both PM$_{10}$ and PM$_{2.5}$. The results of the health assessment showed that the eight heavy metals studied pose significant non-carcinogenic risks and Cr, Cd, and Co pose lifetime lung cancer risks to local residents, especially to children.

Keywords PM$_{10}$ · PM$_{2.5}$ · Heavy metals · Health risk · Baotou

Introduction

Mining activities are notorious for adverse environmental impacts, including pollution, habitat loss, soil erosion, and geological disasters (Salomons 1995; Klukanová and Rapant 1999; Aguilar et al. 2004; Luís et al. 2011). Among these environmental problems caused by mining activities, the production and dispersion of atmospheric particles has become a great concern in recent years (Kaonga and Kgabi 2011; Chen et al. 2013; Serbula et al. 2014). Atmospheric particulates are generated from numerous sources, both natural and anthropogenic, but in areas near mining, mining operations are considered the largest contributor. The processes of mining, such as crushing, grinding, excavating, smelting, and refining, can produce large quantities of particulate matter (PM), containing dangerously high levels of heavy metals (Csavina et al. 2012).

Inhalable particulate matter (PM$_{10}$), particularly fine particles (PM$_{2.5}$), have been shown to cause adverse effects on human health, including asthma, lung cancer, and cardiovascular diseases (Pope et al. 2002; Sanchez et al. 2009). Lung and other organ injuries from atmospheric heavy metal exposure have also been well-documented (Espinosa et al. 2001; Cancio et al. 2008; Leili et al. 2008).
Baotou city, one of the most industrialized cities of northwest China, has very poor air quality due to large-scale mining activities in the area (Zhen 2012). Toxic elements are mobilized and released into the air as particle matter from anthropogenic activities and pose significant health risks to local residents. However, PM$_{2.5}$ and PM$_{10}$ of Baotou has only been monitored in very recent years. Moreover, little work has addressed the association between the concentrations of aerosol metallic elements and adverse health impacts on the local residents.

The objective of this study was to investigate both the total mass and heavy metal concentrations of PM$_{2.5}$ and PM$_{10}$ as well as how these concentrations varied spatially throughout the city. Sampling was performed in four representative areas of Baotou, including a mining area (MA), an industrial area, a residential area (RA), and the city center. This study also aimed at estimating the non-carcinogenic health risks and lifetime cancer risks of heavy metals exposure for local residents.

**Materials and methods**

Description of sampling sites

Baotou is located in the central Inner Mongolia Autonomous Region of China. The city is situated on the Tumochuan and Hetao Plateau, and the Yin Mountains cross the urban area in the central part. The area borders Mongolia to the north, and in the south, the Yellow River runs through the city west to the east for 22 km. Baotou has a cold, semi-arid, continental monsoon climate. The mean annual temperature is 7.2 °C. The annual average rainfall is approximately 310 mm, with the majority mostly occurring in July and August when the southeast monsoon carries rainwater into the province. The prevailing wind direction is northwest, with an average wind speed of 1.2 m s$^{-1}$. Due to the arid climate and large temperature differences between day and night, dust storms frequently occur in this area, especially in spring.

As shown in Fig. 1, four sampling sites of different types of areas were selected in Baotou. The first sampling site was within the Bayan Obo as a representative MA. Bayan Obo is a typical mining region in north Baotou where a large-scale open-cut (rare earth elements)–Fe–Nb pit is located, and large quantities of raw ore are mined. The second sampling site was a typical smelting area (SA) in west Baotou, which was surrounded by numerous chemical and metallurgical factories, refineries, and power plants. This area is the site to which raw ores from Bayan Obo are transported by railroad for further processing. The third sampling site was a city center area (CA), characterized by a highly dense population, heavy traffic, and commercial activities. Finally, the forth sampling site was a representative RA of Baotou, located northeast of the CA.
Sample collection and analysis

PM$_{10}$ and PM$_{2.5}$ samples were collected on quartz microfiber filters (MK360, Munktell, Sweden) using a mid-volume aerosol sampler (LaoYing 2030, Qingdao Laoshan Institute of Applied Technology, Qingdao, China) at a flow rate of 100 L min$^{-1}$. The sampling height was about 1.5 m. At each sampling site, twelve 12-h samples of both PM$_{10}$ and PM$_{2.5}$ were collected within different time periods between July 25, 2013, and August 30, 2013. Meteorological parameters such as wind speed, wind direction, temperature, and humidity were also recorded at the time of sample collection.

All quartz microfiber filters were dried in a desiccator for 48 h. The filters were weighed before and after aerosol sampling to determine the mass of PM$_{10}$ and PM$_{2.5}$. The filters were subsequently sealed in a filter holder and stored at $-20$ °C until analysis.

To prepare samples for measurement of heavy metals concentrations, each filter was cut into fragments. The fragments were placed in a PTFE crucible and then digested in a mixture of HNO$_3$, HClO$_4$, and HF which was heated until about 0.5 mL of colorless solution was obtained. After cooling, the solution was filtered and diluted to a total of 25 mL with Milli-Q water. The concentrations of Cr, Cu, Zn, Pb, and Mn were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 5300 DV, Perkin Elmer), and the concentrations of Cd, Co, and Ni were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, ELAN DRC-e, Perkin Elmer SCIEX). Each measurement was performed in duplicate, and each group had three replicates. National reference samples, replicates, and blanks were also measured to ensure accuracy of the results. The relative error of the results was on average better than 5%.

Risk assessment

Exposure dose

In this study, the risk assessment model developed by the Environmental Protection Agency (EPA) of the United States was used to evaluate the health risks posed by heavy metals in PM$_{2.5}$. Considering the variety of physiological characteristics and living styles of Baotou city residents, we divided them into three groups: male (>16 years), female (>16 years) and children (<16 years). Since metal exposure can occur through direct inhalation, ingestion, and dermal contact, the exposure concentration (EC, μg m$^{-3}$), chemical daily intake (CDI, mg kg$^{-1}$), and dermal absorbed dose (DAD, mg kg$^{-1}$) were calculated to assess total exposure dose. EC, CDI, and DAD were calculated according to the Human Health Evaluation Manual (Part A), Supplemental Guidance for Dermal Risk Assessment (Part E), and Supplemental Guidance for Inhalation Risk Assessment (Part F) (EPA 1989, 2004, 2009). The equations are as follows:

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

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

$$\text{EC} = \frac{C \times \text{ET} \times \text{EF} \times \text{ED}}{\text{AT}} \quad (3)$$

where $C$ stands for the metal concentration in PM$_{2.5}$ (mg kg$^{-1}$ for CDI and DAD, μg m$^{-3}$ for EC). All of the exposure factors for these models are shown in Table 1.

Risk characterization

The hazard quotient (HQ) was calculated based on exposure dose to assess non-carcinogenic risks posed by airborne metals. The equations are as follows:

$$\text{HQ}_{\text{ing}} = \frac{\text{CDI}}{\text{RfDo}} \quad (4)$$

$$\text{HQ}_{\text{inh}} = \frac{\text{EC} \times (1000 \times \text{RfCi} \times 1000 \mu g \text{ mg}^{-1})}{\text{RfDo} \times \text{GIABS}} \quad (5)$$

$$\text{HQ}_{\text{derm}} = \frac{\text{DAD}}{\text{RfDo} \times \text{GIABS}} \quad (6)$$

where RfDo is oral reference dose (mg kg$^{-1}$ day$^{-1}$), RfCi is inhalation reference concentrations (μg m$^{-3}$), and GIABS is the gastrointestinal absorption factor. The RfDo, RfCi, and GIABS values for Cr(VI), Ni (refinery dust), Cu, Cd (diet), Pb, Zn (metallic), Co, and Mn (diet) were used from the screening level tables provided by the US EPA (2014).

The hazard index (HI) is equal to the sum of the HQ values for ingestion, inhalation, and dermal contact and represents the total potential non-carcinogenic risks of different pollutants. An HI <1 indicates that there is no significant risk of non-carcinogenic effects, and when HI is >1, a non-carcinogenic effect is likely to exist (EPA 1989).
Cadmium, Cr and Ni (carcinogens) and Pb and Co (probable carcinogens) were chosen for further evaluations as they were classified as problem chemicals by the International Agency for Research on Cancer (IARC 2014). Based on others’ previous studies (Greene and Morris 2006; Fang et al. 2013), the individual lifetime lung cancer risk ($R_{ic}$) was calculated as follows:

$$R_{ic} = \frac{C \times ED \times IUR}{70 \text{ years}}$$

where $C$ is the contaminant concentration (µg m$^{-3}$) and IUR is the inhalation unit risk as defined by the US EPA Integrated Risk Information System (IRIS). The exposure duration (ED) was 92 days year$^{-1}$ for 70 years in this study. The IUR values for each metal were used from the screening level tables provided by the US EPA (2014).

Due to the fact that heavy metals exposure during childhood may result in a higher lifetime cancer risk than a similar duration exposure during adulthood (EPA 2009), evaluating only $R_{ic}$ may underestimate cancer risks. Thus, it is necessary to take into account age at the time of the exposure. Therefore, age-dependent adjustment factors (ADAFs), as recommended by the US EPA, were used in this study (EPA 2009). Exposure at an age <2 years old requires a tenfold adjustment and at ages 2–16 years old requires a threefold adjustment. No adjustment is needed for exposure at 16 years and older. The equations for lifetime cancer risk were altered to including ADAFs, as follows:

For a baby (0–2 years): $R_b$

$$R_b = R_{ic} \times 10(\text{ADAF}) \times \left(\frac{2 \text{ years}}{70 \text{ years}}\right)$$

(8)

For a child (2–16 years): $R_c$

$$R_c = R_{ic} \times 3(\text{ADAF}) \times \left(\frac{14 \text{ years}}{70 \text{ years}}\right)$$

(9)

For an adult ( > 16 years): $R_a$

$$R_a = R_{ic} \times 1(\text{ADAF}) \times \left(\frac{55 \text{ years}}{70 \text{ years}}\right)$$

(10)

The actual lifetime lung cancer risk ($R$) is the sum of the risk values at each stage in life:

$$R = R_b + R_c + R_a$$

(11)

Cancer risks less than 1 × 10$^{-6}$ are considered negligible by the US EPA.

### Results and discussion

The mass concentrations of PM$_{10}$ and PM$_{2.5}$

The mass concentrations of PM$_{10}$ and PM$_{2.5}$ determined for the four sampling sites in Baotou city are shown in Fig. 2. The average mass concentrations for PM$_{2.5}$ and PM$_{10}$ ranged from 26.4 to 129.2 and 71.2 to 318.3 µg m$^{-3}$, respectively, with the highest concentrations found in SA followed by CA, RA, and MA in
Compared to the Air Quality Standard of China (PM$_{2.5}$ ≤ 75 µg m$^{-3}$ and PM$_{10}$ ≤ 150 µg m$^{-3}$), only SA had concentrations of PM 10 and PM 2.5 that were much higher than the limit values. In MA, low levels of both PM 10 and PM2.5 were found, which may be attributed to the dry climate and strong wind.

The mass concentration ratio of PM 2.5 to PM 10 for MA, SA, CA, and RA were 0.37, 0.41, 0.51, and 0.42, respectively. The average mass concentration ratio was 0.43, meaning that particles between 2.5 and 10 µm contribute to weight more than particles below 2.5 µm. Table 2 summaries several previously reported PM$_{2.5}$/PM$_{10}$ values. Compared to other cities, Baotou had a lower PM$_{2.5}$/PM$_{10}$, indicating a higher coarse particle fraction. Among the different sampling sites, the mass concentration ratios of PM$_{2.5}$ to PM$_{10}$ were ranked in the following order: MA < SA < RA < CA. The highest coarse fraction found in MA may be due to the large quantities of dust produced by excavating associated with mining. CA had a relatively high fraction of fine particles compared to the other sites in Baotou. This may be a result of either heavy traffic in the city center or the wind direction since CA is in the downwind direction of SA, which had the highest level of PM$_{2.5}$.

### Heavy metals concentrations in PM$_{10}$ and PM$_{2.5}$

The heavy metal concentrations in PM$_{2.5}$ and PM$_{10}$ of the ambient air are shown in Fig. 3. The highest heavy metal concentration in PM$_{10}$ and PM$_{2.5}$ were found in SA, followed by CA, RA, and MA. It is worth noting that, contrary to expectations, the metal concentrations in particles from MA, a typically active MA, were the lowest. In order to focus on the composition of the PM, the unit of the metal concentration was changed from “µg m$^{-3}$” to “mg g$^{-1}$.” This change showed that MA now had the highest concentration of metals in PM$_{10}$ and PM$_{2.5}$ (Fig. 4). The low value when expressed as volume was a result of the low PM concentrations in the air. Although low PM$_{2.5}$ concentrations (weight per volume of air) were measured at MA, comparatively high metal content (mg g$^{-1}$) of the collected PM$_{2.5}$ was observed, suggesting that it is an important source of heavy metals.

### Risk assessment

#### Non-carcinogenic risk assessment

HQ and HI for Cr, Ni, Pb, Cd, Cu, Mn, Co, and Zn in PM$_{2.5}$ samples of each site were calculated using the health risk assessment model of the U.S. EPA. In general, the integrated HI for Baotou residents living in any of the four sampling sites were all higher than the safe level (safe level = 1), indicating a rather high...
health risk level from metal exposure in PM$_{2.5}$ (Fig. 5). Residents living in MA and SA faced a higher health risk than residents living in the city center or RA. Among the different groups of residents at the four sites, the integrated HI values increased in the order of male < female < children. The HI values for children were 2–4 times higher than those for adult males and females, indicating that children not only experienced a higher non-carcinogenic risk, but were also more vulnerable to it.

In this study, the HQ values for the three exposure pathways of ingestion, inhalation, and dermal contact varied among the different sites (Fig. 6). There were notable differences between children and adults. For adults in all sampling sites, the HQ values of the three exposure pathways had the same trends: inhalation > ingestion > dermal contact. The average contribution of HQ$_{inh}$ to HI was 62.6 and 60.2 % for adult males and adult females, respectively. However, for children, the HQ$_{ing}$ was the highest, indicating that ingestion was the most health threatening exposure. Additionally, we found that children faced higher health risks through dermal contact than adults. The HQ$_{derm}$ for adult females and males among all sites were all lower than the safe level (=1), meaning there was not a non-carcinogenic risk posed by heavy metals.
Fig. 4  Concentrations of eight metals in a PM$_{2.5}$ and b PM$_{10}$ in Baotou (mg g$^{-1}$) (MA mining area, SA smelting area, CA city center area, RA residential area)

![Bar chart showing concentrations of heavy metals in PM$_{2.5}$ and PM$_{10}$](image)

Table 3  The ratios of metal concentrations in PM$_{2.5}$ to that in PM$_{10}$

| Metal | MA (mining area) | SA (smelting area) | CA (city center area) | RA (residential area) |
|-------|------------------|--------------------|-----------------------|-----------------------|
| Cr    | 1.30             | 1.58               | 1.23                  | 1.54                  |
| Ni    | 1.72             | 0.81               | 0.76                  | 1.17                  |
| Cu    | 1.25             | 4.51               | 1.64                  | 2.58                  |
| Cd    | 1.26             | 3.37               | 1.73                  | 4.47                  |
| Pb    | 1.38             | 1.38               | 2.37                  | 1.10                  |
| Zn    | 1.42             | 2.66               | 1.34                  | 2.70                  |
| Co    | 0.85             | 0.60               | 0.37                  | 0.88                  |
| Mn    | 0.81             | 1.57               | 1.23                  | 2.12                  |
in PM$_{2.5}$. On the contrary, for children, the values of HQ$_{derr}$ were all higher than the safe level and accounted for a larger proportion (20.0% in average for children, 12.1% in average for adults) in the integrated HI values.

HIs for Cr, Mn, Cd, and Pb were notably higher than those for other elements (Table 4). In most places, the HI values for Cr and Mn were close to or higher than the safe level, indicating that in Baotou, they might pose non-carcinogenic health risks to both adults and children. Additionally, we found that the Cr HI for children was 2–3 times higher than that for adults at each site, and therefore, Cr might pose higher potential health risks to children. Except for Cr and Mn, the HIs for each selected metal for both adults and children were mostly within the safety range and ranked in the following order: Pb > Cd > Co > Ni > Cu > Zn for CA site, Cd > Pb > Co > Ni > Cu > Zn for all other sites. The higher HIs for Pb in CA site may be attributed to the heavier traffic burden in the city center. Furthermore, the Pb and Cd HIs for children slightly exceeded the safe level, indicating that Pb and Cd pose potential health risks to children and should be studied more extensively.

**Lifetime cancer risk assessment**

Particulate matter in air, especially in heavily industrialized urban environments, contains a variety of known human carcinogens. In this study, five
carcinogens were investigated. We evaluated the lifetime cancer risks for residents at each site using the mean concentration of each carcinogenic metal in PM$_{2.5}$ and Eq. (11) (Table 5). In all four selected sampling sites in Baotou, the lifetime lung cancer risk was in excess ($>1 \times 10^{-6}$) as posed by the total of five carcinogenic metals (Pb, Cr, Co, Ni and Cd), indicating that carcinogenic risk is not negligible. Among the sites, SA had the highest risks, followed by MA, RA and CA. This indicates that SA residents might face a higher level of cancer risks posed by heavy metals in PM$_{2.5}$.

Among the five selected carcinogenic metals, the cancer risks of Cr, Cd, and Co at all sampling sites were higher than the threshold value $1 \times 10^{-6}$. The leading heavy metal was persistently Cr which posed cancer risks 2–3 orders of magnitude higher than the threshold value as well as those posed by other metals. The lifetime cancer risks of Pb and Ni (all sites except for SA) were lower than $1 \times 10^{-6}$, implying negligible carcinogenic risk estimates.

**Conclusion**

The concentration of PM$_{10}$ and PM$_{2.5}$ at all sampling sites except for the SA industrial site was all below the Air Quality Standard of China. SA had the highest metal concentrations per volume of air, while MA had the highest metal concentrations per mass of particles collected. Zn, Mn, Pb, and Cr were the main metal pollutants in both PM$_{10}$ and PM$_{2.5}$. Most selected heavy metals were enriched in the PM$_{2.5}$ fraction at different sampling sites. For the health assessment, all eight selected heavy metals in PM$_{2.5}$ posed non-carcinogenic risks to all groups of residents. Cr, Cd and Co were the most significant contributors to cancer risks in this assessment. Cr had the highest lifetime cancer risk on residents. We hope these results will help raise focus on enforcing more stringent limitations on industrial emissions. Among different groups of people, children experienced the highest health risk in Baotou, followed by adult females and

| Table 4 | HI values for each non-carcinogenic metal in PM$_{2.5}$ collected in Baotou |
|---------|-----------------------------------|
|         | Adults (male) | Adults (female) | Children |
|         | CA | MA | SA | RA | CA | MA | SA | RA | CA | MA | SA | RA | CA | MA | SA | RA |
| Cr      | 0.59 | 0.62 | 0.63 | 0.66 | 0.72 | 0.72 | 0.72 | 0.72 | 0.72 | 0.72 | 0.72 | 0.72 | 0.72 | 0.72 | 0.72 | 0.72 |
| Ni      | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| Cu      | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| Cd      | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 | 0.29 |
| Pb      | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Mn      | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| Total   | 2.18 | 2.88 | 3.06 | 3.98 | 4.29 | 4.38 | 5.06 | 5.06 | 5.06 | 5.06 | 5.06 | 5.06 | 5.06 | 5.06 | 5.06 | 5.06 |

MA mining area, SA smelting area, CA city center area, RA residential area.
then adult males. Thus, more attention should be paid on protecting children from pollution hazards.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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**Table 5** Lifetime lung cancer risk ($R$ values) of residents in Baotou

|       | MA    | SA    | CA    | RA    |
|-------|-------|-------|-------|-------|
| Cr    | 2.24E−04 | 3.25E−04 | 1.17E−04 | 1.56E−04 |
| Ni    | 7.54E−07 | 1.13E−06 | 6.12E−07 | 6.34E−07 |
| Cd    | 4.25E−06 | 7.66E−06 | 3.35E−06 | 4.55E−06 |
| Pb    | 1.25E−07 | 5.71E−07 | 3.85E−07 | 2.61E−07 |
| Co    | 2.77E−06 | 5.89E−06 | 1.46E−06 | 2.40E−06 |
| Total | 2.32E−04 | 3.40E−04 | 1.22E−04 | 1.64E−04 |

$R$ values higher than safe value ($1 \times 10^{-6}$) are highlighted in bold.

MA mining area, SA smelting area, CA city center area, RA residential area.
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