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ORIGINAL PAPER

Population health risk via dietary exposure to trace elements (Cu, Zn, Pb, Cd, Hg, and As) in Qiqihar, Northeastern China

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Abstract The estimated daily intakes (EDIs) of six trace elements (Cu, Zn, Pb, Cd, Hg, and As) in vegetables (leafy vegetable, i.e., bok choy, fruit vegetables, i.e., cucumber and tomato, and other categories, i.e., mushroom, kidney bean, and potato), cereals (rice and wheat flour), and meats (pork, mutton, and beef) most commonly consumed by adult inhabitants of Qiqihar, Northeastern China, were determined to assess the health status of local people. The average EDIs of Cu, Zn, Pb, Cd, Hg, and As were with 20.77 μg (kg bw)$^{-1}$ day^{-1} of Cu, 288 μg (kg bw)$^{-1}$ day^{-1} of Zn, 2.01 μg (kg bw)$^{-1}$ day^{-1} of Pb, 0.41 μg (kg bw)$^{-1}$ day^{-1} of Cd, 0.01 μg (kg bw)$^{-1}$ day^{-1} of Hg, and 0.52 μg (kg bw)$^{-1}$ day^{-1} of As, respectively, which are below the daily allowance recommended by FAO/WHO. However, the maximum EDIs of Pb and Cd were 4.56 μg (kg bw)$^{-1}$ day^{-1} and 1.68 μg (kg bw)$^{-1}$ day^{-1}, respectively, which are above the recommended levels [i.e., 3.58 μg (kg bw)$^{-1}$ day^{-1} for Pb and 1.0 μg (kg bw)$^{-1}$ day^{-1} for Cd] by FAO/WHO. This finding indicates that the potential health risk induced by daily ingestion of Pb and Cd for the local residents should receive a significant concern. Similarly, we detected elevated Pb and Cd concentrations, i.e., with average of 13.58 and 0.60 mg kg^{-1} dw, respectively, in the adult scalp hairs. Consumption of rice, potato, bok choy, and wheat flour contributed to 75 and 82% of Pb and Cd daily intake from foodstuffs. Nevertheless, human scalp hair is inappropriate biological material for determination of the nutritional status of trace elements in this region.

Keywords Dietary intake · Trace element · Health risk · Human scalp hair · Biomarker

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Introduction

Rapid urbanization and industrialization increase environmental contaminations and thus cause the accumulation of heavy metals, such as Pb and Cd, in various daily foodstuffs of human beings. Excessive ingestion of these trace elements resulted in detrimental physiological effects on human health, e.g., Pb and Cd may persistently harm the kidney, liver, and other vital organs of the human body (Duruibe et al. 2007). Humans are primarily exposed to toxic trace elements via dietary intake (Tripathi et al. 1997; González-Muñz and Meseguer 2008), which accounting for over 90% of total human exposure compared with other routes of environmental exposures (Loutfy et al. 2006). Thus, the assessments of the concentrations and rate of dietary intake trace elements in food products are particularly significant in determining to reveal the risks posed by these heavy metals on human health (Rodrigues et al. 2008).

Cereals (mainly rice and wheat flour), vegetables, and meat are the major dietary components of people in Asia (especially in China) and are the main sources of essential nutrients. In our previous research, we found that residential areas, agricultural lands, and industrial workshops produce increasing amounts of sludge and wastewater (Luo et al. 2013). These waste materials contain toxic contaminants, such as Zn, Pb, and Cd, and are discharged directly into the irrigation system of Qiqihar City (47°21′8″N, 123°54′42″E), which is an important base of cereal manufacturing in China (Fig. 1 a, b). Consequently, the concentrations of these elements increase not only in the soil (Cui et al. 2014; Chen et al. 2015) but also in the entire biota (Luo et al. 2014a). In addition, pesticides and fertilizers containing high amounts of some elements, e.g., Cd and As, have been improperly utilized to increase food production and meet the demand of the expanding population in the past years (Luo et al. 2015). These elements are readily consumed by plant foods and then transferred along the food chain via consumer intake (Zhang et al. 2012a, b). However, the knowledge on the health risks of these elements for consumers remains limited.

Human scalp hair is frequently used to indicate the degree of environmental exposure to various trace elements; this strategy is less invasive, convenient to store and transport, and less hazardous to handle (Schuhmacher et al. 1991; Mikeley et al. 1998; Nowak and Chmielnicka 2000; Frisch and Schwartz 2002; Pereira et al. 2004; Wang et al. 2009). However, the validity of this biomarker in evaluating the levels of trace elements in human body remains debatable, considering the constraints of exogenous contamination and lack of correlations of trace elements with kidney and liver (Frisch and Schwartz 2002; Rodrigues et al. 2008; González-Muñz and Meseguer 2008).

The present work aims to assess the daily intake of six trace elements (Cu, Zn, Pb, Cd, Hg, and As) through frequently consumed food products in Qiqihar City, Northeastern China. Additionally, the scientific issue of the feasibility of using human scalp hair as a suitable indicator for the toxic risk levels of these trace elements is discussed.

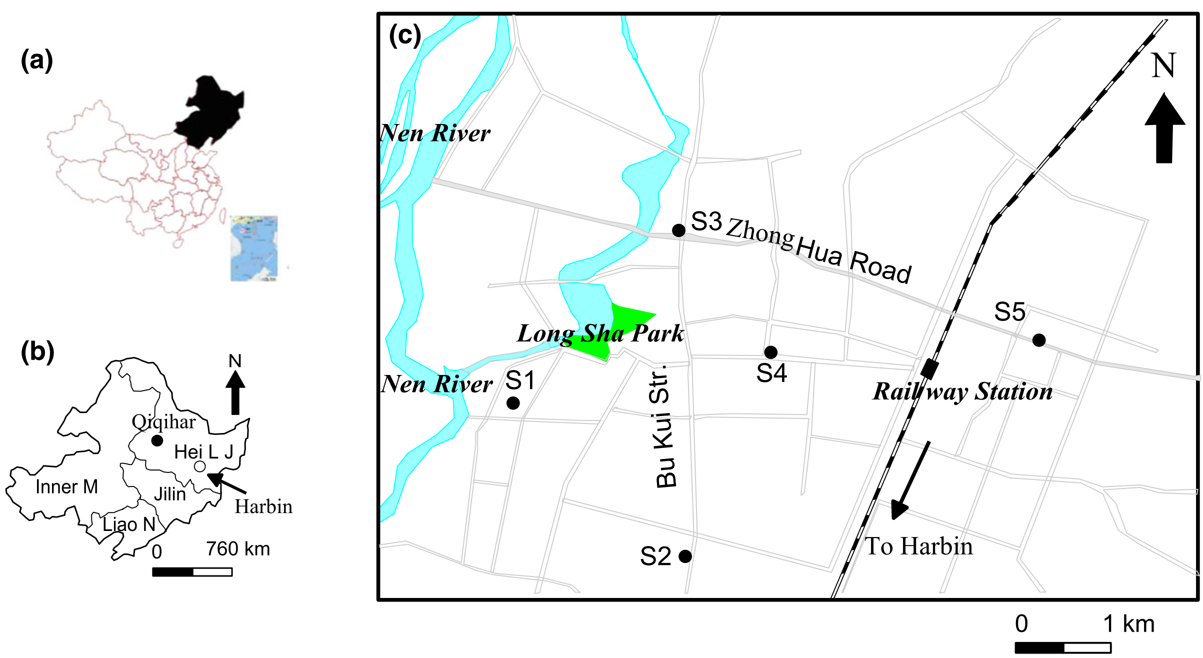

Fig. 1 Location of Qiqihar City (**a**, **b**) and sampling design (**c**)

Materials and methods

Sampling scheme

Qiqihar is an important heavy industrial and cereal base in China. The volume of wastewater discharge (containing Pb, Cd, and other toxic elements) in this region increased from 0.17×10^8 m^3 in 1993 to 0.45×10^8 m^3 in 2010; this considerable increase resulted in profound ecological effects on the local biosphere (Luo et al. 2014a). In the present study, samples of three categories of meat (i.e., pork, mutton, and beef), two categories of cereals (i.e., rice and wheat flour), and six categories of vegetables [i.e., two fruit vegetables: cucumber (*Cucumis sativus* L. var. sativus) and tomato (*Lycopersicon esculentum* mill.); one leafy vegetable: bok choy (*Brassica rapa* var.); one tuberous vegetable: potato (*Solanum tuberosum*); and other commonly consumed vegetables, such as mushroom (*Lentinus edodes* (Berk.) sing) and kidney beans (*Lablab purpureus* (Linn.) Sweet)] were collected at five supermarkets in Qiqihar City in May 2016 (Fig. 1c). These samples were analyzed to monitor the dietary health risks of the trace elements for the local residents. The fresh meat and vegetable samples were immediately transported under refrigeration to the laboratory. In addition, 80 scalp hair samples from four categories of people (male versus female and young versus middle aged) were collected from a barbershop in the vicinity of each supermarket. The hair samples were cut with stainless scissors from the participants, and information regarding their age, gender, and residence status (local resident or not) was collected. The samples were placed under refrigeration and transported back to the laboratory.

The vegetables were thoroughly rinsed with distilled water to remove any pollutants attached on the surface. Prior to acid digestion, the scalp hair samples were cut into small pieces (approximately 3 mm) and washed thrice with deionized water and acetone (extra pure) according to the method by Pereira et al. (2004). The washed hair samples were oven dried to constant (48 h at 60 °C). The dried samples (mainly vegetables) were ground to homogenous powders in a quartz bowl for acid digestion.

Approximately 1–2 g of fresh samples (i.e., meats and vegetables), 0.5 g of cereal samples (i.e., rice and wheat flour), and adult scalp hair were collected for acid digestion.

Microwave digestion and element analysis

Each sample was acid digested in a microwave in accordance with Allen et al. (1986) methods. The techniques used in our study were described by Luo et al. (2014a). Triplicate subsamples of known weight were digested in acid mixture (5 mL HNO_3 + 1 mL H_2SO_4 + 1 mL $HClO_4$) in a closed Teflon crucible and evaporated slowly to almost dryness (at 80 °C), and the residue was dissolved in 5 mL 1:1 diluted HCl and then maintained to 25 mL with deionized water for analysis after the solution has been cooled down to room temperature. The Cu, Zn, Pb, Cd, and As concentrations in the four sample types (three kinds of foodstuffs plus hair samples) were determined through inductively coupled plasma-mass spectrometry (Agilent 7500ce, Agilent Technologies, Inc., Santa Clara, CA, USA). We estimated the precision and accuracy of the analyses based on a certified reference material: *Pseudosciaena crocea* (GBW08573; Beijing Shiji Ouke Bio-tech Co., Ltd) for Cu (1.36 ± 0.13 mg kg^{-1}), Zn (28.8 ± 1.4 mg kg^{-1}), Pb (8.8 ± 1.10 mg kg^{-1}), Cd (0.014 ± 0.001 mg kg^{-1}), and As (5.08 ± 0.39 mg kg^{-1}). The results agreed with the certified values for all metals, with average recovery rates of 102, 94, 103, 105, and 102% for Cu, Zn, Pb, Cd, and As, respectively. We determined the T–Hg concentration in these samples by using a mercury analyzer (Tekran 2600 CVAFS, Tekran Instrument Corporation, Knoxville, USA) in accordance with the methods described in our previous study (Luo et al. 2014b). The detection limit for all elements was 5 ng kg^{-1}. Reusable materials, such as Petri dishes, were acid washed. The samples were analyzed in triplicate at a relative standard deviation lower below 1.5%.

Estimation of dietary exposure to heavy metals

The estimated daily intake (EDI) of heavy metals was determined to assess the dietary exposure of the locals; EDI was expressed as the following empirical equation:

$$\mathrm{EDI} = F_{\mathrm{IR}} \times C/\mathrm{B.W.}, \quad (1)$$

where *EDI* is the daily intake of a given chemical from an individual food item [μg (kg body weight)$^{-1}$ day^{-1}, μg (kg bw)$^{-1}$ day^{-1})], F_{IR} is the mean food intake in each day (g day^{-1}), C is the concentration of heavy metals in each food product (mg kg^{-1} fw), and B.W. represents the reference body weight (kg). Following the work of Zheng et al. (2007), we set the average body weight of the locals to 56 kg. The element concentrations in the rice and wheat flour were converted with a factor of 0.86, because home-stored rice commonly contains approximately 14% water.

Statistical analysis

The participants (20–50 years of age based on the information recorded in the questionnaire) were categorized into two classes in accordance with age (i.e., juvenile, age 21–35 years ($n = 44$); and middle aged, age 36–50 years ($n = 36$). The correlation coefficients of metal concentrations in the scalp hair and food stuffs (i.e., hair versus meats, hair versus cereals, and hair versus vegetables) were computed based on the average metal concentrations in the samples. Before statistical analyses, the logarithmic transformation of the data was performed if they did not meet the assumption of normality distribution. SPSS 10.0 for Windows was used for data analysis.

Results

Trace elements in food products

Tables 1 and 2 show the concentrations of six trace elements in the selected food products collected within the study area. The average concentrations of Cu, Hg, and As in the three categories of food products most frequently consumed by the local residents were generally below the safety level given by WHO/FAO (2011). According to WHO/FAO (2011), the safety level for Zn in most frequently consumed food products is 26 mg kg^{-1}. The Zn concentrations in most of the food categories tested in the current work were above the safe level. The average concentrations of Pb in pork [0.23 mg kg^{-1} fresh weight (fw)], rice [0.24 mg kg^{-1} dry weight (dw)], peel of cucumber (0.16 mg kg^{-1} fw), tomato (0.15 mg kg^{-1} fw), potato (0.35 mg kg^{-1} fw), and leafy vegetable bok choy (0.34 mg kg^{-1} fw) exceeded the safety levels suggested by WHO/FAO (2011). The maximum Pb concentration (0.51 mg kg^{-1} fw) in the kidney bean also exceeded the threshold level. The average Cd concentrations in the cucumber and potato peels and

Table 1 Concentrations of six trace elements in meat and food products (mg kg^{-1}, $n = 5$, fw)

	Cu	Zn	Pb	Cd	Hg	As
Meat						
Pork	2.21 ± 0.36 (1.92–2.52)	**66.91** ± 18.94 (**48.10–89.31**)	**0.23** ± 0.11 (0.05–**0.34**)	0.05 ± 0.03 (0.02–0.09)	0 (ND)	0 (ND)
Mutton	2.88 ± 1.48 (1.63–4.86)	**48.90** ± 14.74 (25.80–**65.83**)	0.18 ± 0.05 (0.12–0.24)	0.03 ± 0.02 (0.01–0.06)	0 (ND–**0.07**)	0 ND
Beef	2.67 ± 2.23 (0.92–6.56)	**53.14** ± 21.21 (**37.05–80.44**)	0.17 ± 0.12 (0.00–0.29)	0.02 ± 0.01 (0.00–0.04)	0 (ND)	0 (ND)
Cereal						
Rice	2.37 ± 1.19 (0.43–3.03)	**34.29** ± 14.03 (15.04–**50.45**)	**0.24** ± 0.13 (0.04–**0.40**)	0.03 ± 0.04 (ND–**0.11**)	0 (ND)	0.13 ± 0.12 (ND–0.26)
Wheat flour	4.31 ± 1.17 (3.36–6.25)	**32.45** ± 21.82 (13.24–**68.44**)	0.06 ± 0.05 (ND–0.14)	0.06 ± 0.06 (ND–**0.14**)	ND (ND)	ND (ND)
WHO/FAO (2011)	10	26	0.20	0.20–0.40	0.05	0.50

"ND" means the concentration means below the detection level; the bold figure represents the concentration exceeded the safe limit suggested by WHO/FAO (2011)

Table 2 Concentrations of six elements in the vegetable samples (mg kg^{-1}, $n = 5$, fw)

	Cu	Zn	Pb	Cd	Hg	As
Fruit vegetable						
Cucumber						
Peel	0.51 ± 0.31 (0.05–0.91)	23.08 ± 6.82 (14.77–**30.32**)	**0.16** ± 0.13 (0.04–**0.31**)	0.05 ± 0.06 (ND–**0.14**)	0.00 (ND)	0.00 (ND–0.15)
Core	1.15 ± 1.08 (0.11–2.41)	15.66 ± 3.38 (11.43–19.27)	0.07 ± 0.03 (0.03–**0.11**)	0.03 ± 0.02 (ND–0.04)	0.00 (ND)	0.00 (ND–0.13)
Tomato						
Peel	1.03 ± 0.52 (0.59–1.80)	24.13 ± 11.55 (10.12–**37.67**)	**0.15** ± 0.08 (0.05–**0.24**)	0.02 ± 0.01 (ND–0.04)	0.00 (ND–**0.03**)	0.05 ± 0.69 (ND–0.24)
Tuber	0.58 ± 0.31 (0.05–0.84)	15.73 ± 5.49 (8.16–22.05)	0.07 ± 0.05 (0.00–**0.14**)	0.02 ± 0.02 (ND–0.02)	0.00 (ND)	0.00 (ND)
WHO/FAO (2011)	10	26	0.10	0.05	0.01	0.20
Mushroom						
Root	1.11 ± 0.61 (0.23–1.36)	2.63 ± 0.66 (1.89–3.54)	0.31 ± 0.37 (0.07–0.93)	0.09 ± 0.07 (ND–0.16)	0.00 (ND)	0.00 (ND)
Stem	1.86 ± 1.02 (1.05–3.58)	3.90 ± 1.31 (1.94–4.83)	0.30 ± 0.21 (0.11–0.62)	0.08 ± 0.07 (ND–0.19)	0.00 (ND)	0.00 (ND)
WHO/FAO (2011)	10	26	1.00	0.20	0.10	0.50
Bok choy (leafy vegetable)						
Leaf	1.08 ± 0.30 (0.71–1.39)	**31.40** ± 9.77 (21.45–**44.8**)	**0.34** ± 0.21 (0.13–**0.63**)	0.07 ± 0.09 (0.02–**0.23**)	0.00 (ND)	0.00 (ND)
Stem	0.58 ± 0.49 (0.12–0.64)	21.27 ± 6.26 (15.32–**31.28**)	0.28 ± 0.19 (ND–**0.43**)	0.08 ± 0.11 (ND–**0.24**)	0.00 (ND)	0.00 (ND)
Kidney beans						
Beans	0.62 ± 0.49 (0.00–1.25)	12.22 ± 3.31 (8.08–16.33)	0.25 ± 0.18 (0.06–**0.51**)	0.08 ± 0.13 (ND–**0.27**)	0.00 (ND)	0.00 (ND)
Seed	3.24 ± 0.95 (2.21–4.62)	22.54 ± 7.35 (14.05–**33.92**)	0.13 ± 0.10 (ND–0.24)	0.04 ± 0.05 (ND–0.11)	0.00 (ND)	0.00 (ND)
WHO/FAO (2011)	10	26	0.30	0.20	0.01	0.15
Potato						
Peel	0.32 ± 0.13 (0.15–0.45)	15.82 ± 8.70 (7.17–**29.62**)	**0.35** ± 0.16 (0.15–**0.55**)	0.08 ± 0.11 (ND–0.25)	0.00 (ND–**0.04**)	**0.37** ± 0.59 (ND–**1.40**)
Tuber	0.14 ± 0.09 (0.04–0.28)	15.84 ± 6.03 (7.04–23.65)	0.20 ± 0.14 (0.06–**0.39**)	0.07 ± 0.10 (ND–**0.22**)	0.00 (ND–**0.02**)	0.00 (ND–0.27)
WHO/FAO (2011)	10	26	0.20	0.10	0.01	0.20

The bold figure represents the concentration exceeded the safe limits suggested by WHO/FAO (2011) the maximum Cd concentrations in cereals (i.e., rice and wheat flour), bok choy, and kidney beans exceeded the threshold levels by WHO/FAO (2011). In general, the Hg and As concentrations in most of the selected food products were below detection levels. And the average As concentrations detected in the rice and potato were 0.13 and 0.37 mg kg^{-1} fw, respectively. The maximum Hg concentrations in the mutton, tomato, and potato were above the safety level, with the respective concentrations of 0.07, 0.03, and 0.04 mg kg^{-1} fw. Interestingly, the metal concentrations in different sections of the vegetables varied in the order of peel > core (in cucumber, tomato, and potato) leaf > stem (in the leafy vegetable bok choy).

EDI of trace elements

The EDIs of the six trace elements were calculated based on the average concentrations of the most frequently consumed food products to assess the health risks of the locals from the heavy metal contamination of foods (Table 3). The general trends of EDIs for heavy metals in the selected food products generally followed the order of Zn > Cu > Pb > As > Cd > Hg as well as cereals > pork > leafy vegetable (bok choy) > other vegetables. The highest EDIs of Cu (11.6 μg (kg bw)$^{-1}$ day^{-1}) and Zn (127 μg (kg bw)$^{-1}$ day^{-1}) were associated with the consumption of wheat flour; moreover, the highest EDIs of Pb (0.94 μg day^{-1}) and Cd (0.27 μg day^{-1}) were attributed to the intake of mushroom and kidney beans, respectively. Nevertheless, Zn, Pb, and Cd were found in the rice and wheat flour at average EDIs of 76.39, 0.53, and 0.09 μg (kg bw)$^{-1}$ day^{-1}, respectively.

The total EDIs of each element in the selected food products were below the daily allowance, as detailed in the following: 20.77 μg (kg bw)$^{-1}$ day^{-1} of Cu, 288 μg (kg bw)$^{-1}$ day^{-1} of Zn, 2.01 μg (kg bw)$^{-1}$ day^{-1} of Pb, 0.41 μg (kg bw)$^{-1}$ day^{-1} of Cd, 0.05 μg (kg bw)$^{-1}$ day^{-1} of Hg, and 0.52 μg (kg bw)$^{-1}$ day^{-1} of As. Nevertheless, the maximum EDIs of Pb and Cd were 4.56 μg (kg bw)$^{-1}$ day^{-1} and 6.18 μg (kg bw)$^{-1}$ day^{-1}, respectively, which are above the oral reference dose [i.e., 3.57 μg kg^{-1} day^{-1} for Pb and 1.0 μg kg^{-1} day^{-1} for Cd according to FAO/WHO (1997)]. The EDI of As in the local residents was mainly attributed to the consumption of rice and potato. The EDIs of Hg [0–0.2 μg (kg bw)$^{-1}$ day^{-1}] and As [0.52 μg (kg bw)$^{-1}$ day^{-1}] in the local population were well below the recommended dietary values [5 μg (kg bw)$^{-1}$ day^{-1} for Hg and 3.0 μg (kg bw)$^{-1}$ day^{-1} for As according to FAO/WHO (1997)].

The main contributors to the total intake of Cu and Zn were rice and wheat flour, amounting to 56 and 43%, respectively (Table 4). The EDIs of Pb were mainly contributed by rice, with an average of 27% of the total Pb consumption, followed by mushroom (16%), potato (15%), bok choy (14%), and other food products (<15%). Similarly, Cd intake was mainly via wheat flour consumption, amounting to 22% of the total EDIs, followed by mushroom (17%), rice (16%), potato (16%), and kidney bean (12%).

Trace elements in scalp hair

The concentrations of the six trace elements in the scalp hair samples are presented in Table 5. In general, the metal concentrations followed the order of Zn > Cu > Pb > Cd > Hg > As. The essential trace element Zn was predominant in the hair, with concentrations ranging from 128 to 280 mg kg^{-1} dw. The level of Cu in the hair at five sites varied from 15.1 to 30.6 mg kg^{-1} dw and followed the order of male > female in both juvenile and middle-aged groups. High Pb and Cd concentrations were also detected in the hair samples, ranging from 7.46 to 24.9 mg kg^{-1} dw and from 0.35 to 0.92 mg kg^{-1} dw, respectively; the concentrations of these elements followed the order of male < female and juvenile group < middle-aged group. In addition, the scalp hair samples at site S4 contained some Hg; this group mainly consisted of females of the juvenile population. Similarly, the level of As detected in the hair samples at each site ranged from 0.08 to 0.29 mg kg^{-1} dw.

Table 6 shows the correlations of the concentrations of the six trace elements between the hair samples and the three categories of food products, i.e., hair versus meat, hair versus cereal, and hair versus vegetable group. Traces Cu and Cd exhibited a statistically significant linear relationship in the pair of hair versus cereal ($p < 0.05$). Other trace elements, such as Zn, Pb, Hg, and As, did not show any significant linear correlations in the three pairs, i.e., hair versus meat, hair versus cereal, and hair versus vegetable group.

Table 3 Estimated daily intake of six trace elements via three categories of food consumptions [ug $(kg\ bw)^{-1}\ day^{-1}$]

Food consumption ($g\ day^{-1}$)[a]		Cu	Zn	Pb	Cd	Hg	As
Meat							
Pork	42	1.51 (1.42–1.86)	45.61 (36.25–65.95)	0.16 (0.04–0.25)	0.03 (0.01–0.07)	0.00 (ND)	0.00 (ND)
Mutton	13	0.85 (0.37–1.10)	14.44 (5.86–14.96)	0.05 (0.03–0.06)	0.01 (0.00–0.02)	0.00 (0.00–0.02)	0.00 (0.00)
Beef	10	0.79 (0.16–1.11)	15.69 (6.31–13.71)	0.05 (0.00–0.05)	0.01 (0.00–0.01)	0.00 (0.00)	0.00 (0.00)
Cereal							
Rice	139	5.28 (0.80–6.63)	76.39 (27.92–93.66)	0.53 (0.07–0.74)	0.07 (0.00–0.19)	0.00 (0.00–0.06)	0.29 (0.00–0.48)
Wheat flour	96	6.40 (6.24–11.60)	48.19 (24.91–127)	0.09 (0.00–0.26)	0.09 (0.00–0.26)	0.00 (0.00)	0.00 (0.00)
Vegetable							
Mushroom	35	1.50 (0.17–3.61)	3.30 (1.40–5.34)	0.31 (0.05–0.94)	0.07 (0.00–0.19)	0.00 (0.00)	0.00 (0.00)
Bok choy	62	0.84 (0.09–1.40)	26.58 (11.31–45.2)	0.28 (0.00–0.64)	0.01 (0.00–0.24)	0.00 (0.00)	0.00(0.00)
Kidney bean	40	1.95 (0.00–4.66)	17.54 (5.97–34.23)	0.17 (0.00–0.52)	0.05 (0.00–0.27)	0.00 (0.00)	0.00 (0.00)
Cucumber	52	0.62 (0.04–2.43)	19.55 (8.44–30.59)	0.03 (0.02–0.31)	0.01 (0.00–0.14)	0.00 (0.00–0.02)	0.00 (0.00)
Tomato	60	0.81 (0.04–1.82)	4.03 (6.10–38.01)	0.02 (0.00–0.24)	0.00 (0.00–0.05)	0.00 (0.00–0.12)	0.00 (0.00–0.24)
Potato	85	0.23 (0.03–0.45)	16.96 (5.20–29.89)	0.30 (0.04–0.56)	0.06 (0.00–0.25)	0.00 (0.00–0.04)	0.23 (0.00–1.41)
Sum	634	20.77 (9.54–36.69)	288 (176–498)	2.01 (0.33–**4.56**)	0.41 (0.02–**1.68**)	0.00 (0.00–0.20)	0.52 (0.00–2.37)

[a] Based on the study of dietary intake and nutritional pattern of residents in Heilongjiang Province of China by Zhang et al. (2012a, b); the bold figure represents EDI of the trace element exceeded the reference standard [Pb: 3.58 μg $(kg\ bw)^{-1}\ day^{-1}$; Cd: 1.00 μg $(kg\ bw)^{-1}\ day^{-1}$] by FAO/WHO (1997)

Table 4 Contribution (%) of various food items for the six trace elements' daily intake

Food item	Cu	Zn	Pb	Cd	Hg	As
Meat						
Pork	7.25	**15.82**[a]	7.84	8.25	–	0.00
Mutton	4.10	5.01	2.64	2.42	–	0.00
Beef	3.79	5.44	2.57	1.86	–	0.00
Sum	15.14	26.27	13.05	12.53	–	0.00
Cereal						
Rice	**25.42**	**26.50**	**26.66**	**16.34**	–	**55.51**
Wheat flour	**30.82**	**16.72**	4.44	**21.79**	–	0.00
Sum	56.24	43.22	31.10	38.12	–	55.51
Vegetable						
Mushroom	7.24	1.14	**15.60**	**17.27**	–	0.00
Bok choy	4.03	9.22	**14.09**	2.47	–	0.00
Kidney bean	9.38	6.08	8.55	**12.34**	–	0.00
Cucumber	2.96	6.78	1.51	2.47	–	0.00
Tomato	3.89	1.40	1.01	0.00	–	0.00
Potato	1.12	5.88	**15.09**	**14.80**	–	**44.49**
Sum	28.62	30.51	55.85	49.34	–	44.49

[a] The bold figure represents main contribution to EDIs of the certain trace element

Discussion

The present study reveals two important findings about the health risk posed by trace elements via most frequently consumed foodstuffs to the people of Qiqihar, Northeastern China. To be first, the ingestion rates of Pb and Cd via the food products by the locals were as unsafe and should be given close attention. Secondly, human scalp hair is an invalidity biomarker for evaluating the nutritional status of trace elements, i.e., Cu, Zn, Pb, Cd, Hg, and As in this region.

The leafy vegetable bok choy accumulated higher Pb and Cd concentrations compared with the non-leafy vegetables, such as cucumber, tomato, and kidney bean. This finding agrees with previous reports (Tripathi et al. 1997; Muchuweti et al. 2006; Zhuang et al. 2009). The high translocation, high transpiration, and fast growth rates of leafy vegetables may facilitate the intake of these elements. In addition, leafy vegetables are susceptible to physical contamination via soil dust and splash because of expanding foliar surface areas. Unlike those of the leafy vegetables, the high EDIs of cereals, i.e., rice and wheat flour as staple food in China, were mainly caused by their large consumption rate among the daily food products (Tripathi et al. 1997; Lee et al. 2006; Zheng et al. 2007; Singh et al. 2010), as well as the uptake of these trace elements from the soil according to Liu et al. (2005) and Singh et al. (2010).

In this research, the daily intake of Zn via the selected food products did not pose an obvious potential health risk to the local residents (Table 7), because the EDIs of this element (with an average of 288 μg (kg bw)$^{-1}$ day^{-1}) did not exceed the recommended level (300–1000 μg (kg bw)$^{-1}$ day^{-1}) according to FAO/WHO (1997). In addition, the EDI

Table 5 Six trace elements enrichment in the hair samples at five sites and different sex and age (mg kg^{-1}, dw)

	Cu	Zn	Pb	Cd	Hg	As
Sampling site (n = 16)						
S1	30.60 ± 7.28	280 ± 117[a]	14.96 ± 5.24[a]	0.78 ± 0.41[a]	ND	0.13 ± 0.14
S2	16.30 ± 10.35	128 ± 67[a]	7.46 ± 7.02	0.35 ± 0.33	ND	0.13 ± 0.17
S3	19.40 ± 7.24	226 ± 135[a]	10.44 ± 9.27[a]	0.52 ± 0.50[a]	ND	0.07 ± 0.03
S4	15.10 ± 9.57	192 ± 108[a]	10.12 ± 15.36[a]	0.58 ± 0.74[a]	0.57 ± 0.25	0.08 ± 0.11
S5	17.50 ± 3.79	239 ± 145[a]	24.90 ± 14.50[a]	0.76 ± 0.5[a]	ND	0.29 ± 0.32
Juvenile (n = 44)						
Female	18.8 ± 10.7	225 ± 116[a]	14.59 ± 13.28[a]	0.84 ± 0.47[a]	0.53 ± 0.42	0.05 ± 0.03
Male	22.1 ± 8.6	208 ± 138[a]	8.75 ± 4.45	0.47 ± 0.27	ND	0.21 ± 0.26
Middle aged (n = 36)						
Female	14.41 ± 9.56	237 ± 127[a]	18.68 ± 16.49[a]	0.92 ± 0.74[a]	ND	0.31 ± 0.27
Male	22.65 ± 4.75	190 ± 42[a]	13.57 ± 13.42[a]	0.76 ± 0.43[a]	ND	0.15 ± 0.12

[a] Represents the figure exceeded the average hair level in China (i.e., Zn: 170 mg kg^{-1} dw, Pb: 10 mg kg^{-1} dw, Cd: 0.5 mg kg^{-1} dw; Qing 2004)

Table 6 Pearson correlation coefficients of the selected four trace elements between scalp hair and other three kinds of foods

	Cu	Zn	Pb	Cd	Hg	As
Hair versus meat	−0.38	−0.20	0.39	0.09	–	–
Hair versus cereal	0.71*	0.24	0.44	0.60*	–	0.44
Hair versus vegetable	−0.47	0.54	−0.22	0.40	–	0.37

* Correlation is significant at the 0.05 level

Table 7 Comparison of EDIs of six elements with other regions [ug (kg bw)$^{-1}$ day^{-1}]

	Cu	Zn	Pb	Cd	Hg	As
In this paper	20.77 (9.54–36.69)	288 (176–498)	2.01 (0.33–**4.56**)	0.41 (0.02–**1.68**)	0.00 (0.00–0.20)	0.52 (0.00–2.37)
Huludao of China (Zheng et al. 2007)	48.73	219	1.46	0.75	0.04	–
Beijing of China (Song et al. 2009)[a]	3.14	15.7	0.28	0.06	–	0.08
Mine area of Shaoguan China (Zhuang et al. 2009)[b]	41.47	240	8.77	5.66	–	–
Bombay of India (Tripathi et al. 1997)	26.14	187	0.44	0.08	–	–
Korean (Lee et al. 2006)	–	–	0.44	0.26	0.03	0.70
Rio de Janeiro of Brazil (Santos et al. 2004)	20.00	85.71	0.50	0.03		
FAO/WHO (1997)	50–500	300–1000	3.58	1.00	5.00	50.00

The bold figure represents EDI of the trace element exceeded the reference standard by FAO/WHO (1997)

[a] EDI only through vegetable intake and [b] the EDI was sum of rice and vegetable

of Zn did not exceed the levels reported in other places, in contrast to the conclusions of Tripathi et al. (1997), Zheng et al. (2007), and Zhuang et al. (2009), Table 7). Similarly, the EDIs of Cu, Hg, and As were lower than the recommended standards by FAO/WHO (1997); hence, the intake levels of these elements do not pose a health concern for local inhabitants. Nevertheless, high concentrations of Pb and Cd in food products (namely cereals and vegetables) and their high intake rates resulted in high EDIs for the locals; that is, the average EDIs of Pb and Cd were above the levels reported in Beijing, China; Bombay, India; Korea; and Rio de Janeiro, Brazil. The maximum EDIs of Pb (4.56 μg (kg bw)$^{-1}$ day^{-1}) and Cd (1.68 μg (kg bw)$^{-1}$ day^{-1}) exceeded the recommended levels [i.e., 3.58 μg (kg bw)$^{-1}$ day^{-1} for Pb and 1.0 μg (kg bw)$^{-1}$ day^{-1} for Cd] by FAO/WHO (1997). Thus, the ingestion rates of Pb and Cd via the food products by the locals were regarded as unsafe and should be given close attention.

In this work, Cu, Hg, and As in the sampled hairs were below the average levels in China and similar to those in other countries (Table 8). The Zn concentration in the hair samples exceeded the average level in China (213 vs. 170 mg kg^{-1}) but was similar to the level in other places without obvious Zn exposure (Table 8). A low Zn content is commonly considered as essential to human metabolism (Afridi et al. 2006). Thus, the Zn level in the scalp hair was considered to be safe. By contrast, the levels of Pb and Cd in the hair samples were obviously larger than the average levels in China and exceeded the levels in Rio de Janeiro of Brazil (Mikeley et al. 1998) and Alcalá University in Spain (González-Muñz and Meseguer 2008). Moreover, the level of Cd in the hair samples was found to be similar to that in Corte do Pinto of Portugal (an abandoned mine area polluted by Pb and Cd; Pereira et al. 2004). Thus, the exposure of the locals to Pb and Cd must be monitored; furthermore, effective measures should be established to reduce Pb and Cd contents in food products for the sake of the health of local residents.

The hair samples in the middle-aged group (25–50 years of age) were prone to contain Pb and

Table 8 Comparison of six elements enriched in the scalp hairs of adult in different regions (mg kg^{-1}, dw)

	Cu	Zn	Pb	Cd	Hg	As
In this paper	19.78 (15.1–30.6)	213 (192–280)	13.58 (7.16–24.90)	0.60 (0.35–0.78)	0.11 (ND–0.57)	0.14 (0.13–0.29)
Avera in China (Qing 2004)	50	170	10.00	0.50	1.50	1.00
Rio de Janeiro of Brazil (Mikeley et al. 1998)	(10–32)	(140–239)	9.30	0.30	2.30	0.15
Corte do Pinto of Portugal (an abandoned mine area polluted by Pb and Cd) (Pereira et al. 2004)	11.63 (0.31–25.33)	282 (69–526)	–	0.62 (0.19–2.49)	–	0.53 (0.05–2.52)
In Pakistan (Afridi et al. 2006)	11.46 (7.81–15.11)	206 (192–220)	6.08 (3.65–8.51)	1.06 (0.25–1.87)	–	–
Alcalá University in Spain (González-Muñz and Meseguer 2008)	(12.47–23.34)	(145–161)	(0.27–1.46)	(0.02–0.03)	(1.80–2.16)	(0.00–0.01)

Cd. Female hair was also more susceptible to Pb and Cd in comparison with male hair. These findings are consistent with previous reports (Schuhmacher et al. 1991; Pereira et al. 2004; González-Muñz and Meseguer 2008). In the work of Pereira et al. (2004), Cd intake in the hair of people aged 26–45 years was significantly higher than that in the hair of people aged <26 and >45 years. In the works of Schuhmacher et al. (1991) and González-Muñz and Meseguer (2008), Pb content was higher in the female group of young adults than in the male group with similar ages, i.e., 10.54 versus 6.55 and 1.46 versus 0.27 mg kg^{-1}, respectively. The levels of metals (Pb and Cd) in human hair could increase over time because most female groups prefer maintaining their long hair for years. However, further research is recommended to verify this speculation.

For most people, the main route of exposure to toxic elements is through diet, as mentioned in the previous section. Consequently, information concerning dietary intake is of utmost importance in the effort to assess the risks of exposure to toxic elements to human health. The use of human scalp hair as a biomarker offers many advantages, including minimal invasiveness, great convenience in storage and transport, and minimal hazard in handling; thus, this method can be employed frequently to assess wildlife and human exposure to different contaminants present in the environment (Schuhmacher et al. 1991; Mikeley et al. 1998; Nowak and Chmielnicka 2000; Frisch and Schwartz 2002; Pereira et al. 2004; Wang et al. 2009). However, human scalp hair is limited by certain factors, i.e., exogenous contamination (Frisch and Schwartz 2002), and its trace elements cannot be correlated with those of other target organs (kidney and liver; González-Muñz and Meseguer 2008); thus, its application is constrained to reflect the degree of authentic environmental exposure. In the present study, the intake of trace elements was not significantly correlated with the levels in the hair samples. Hence, the use of hair samples to determine the environmental exposure of locals to selected trace elements, i.e., Cu, Zn, Pb, Cd, Hg, and As, merits further development.

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