RESEARCH ARTICLE

Risk assessment of heavy metals in air, water, vegetables, grains, and related soils irrigated with biogas slurry in Taihu Basin, China

Bo Bian · Ling Jun Zhou · Lei Li · Lin Lv · Ya Min Fan

Abstract Metal contamination in farmlands irrigated with biogas slurry is of great concern because of its potential health risks to local inhabitants. Health risks that depend heavily on multi-pathway exposure to heavy metals (e.g., Pb, Cd, Cr, Zn, Cu, and As) in water, soil, air, and local food were studied through field sampling in Taihu Basin, China. Results show that Zn, Pb, and Cd in soils irrigated with biogas slurry exceed the soil quality standard values, and grown vegetables and grains contaminated with Pb and Cd exceed the permissible limits. Food ingestion plays an important role in the total average daily dose of metals, especially for Cu and Zn, which account for 94 and 91 %, respectively. Non-carcinogenic risks posed to adults mainly result from Cu, Zn, Pb, Cd, and As through food ingestion and from Cr through soil ingestion. The highest non-carcinogenic risk was determined from food ingestion, followed by soil ingestion, air inhalation, air ingestion, and dermal contact with air. Carcinogenic risks to adults are 6.68 to 7.00 times higher than the safe level and can be attributed to Cr, As, and Cd pollution. The estimated risks mainly result from As and Cd through food ingestion and from Cr through soil ingestion. Both cancer and non-cancer risks through dermal contact can be ignored. Therefore, attention should be paid to health risks imposed by adults' multi-pathway exposure to heavy metals in vegetables, grains, and related soils irrigated with biogas slurry in Taihu Basin. Effective measures should be implemented to control heavy metal pollution and protect potentially exposed adults.

Keywords Heavy metal contamination · Various media · Multi-pathway exposure · Adults · Health risk

Introduction

Heavy metal pollution has long been a concern because of the lack of biodegradability of heavy metals and the toxicity they pose to plants, animals, and human beings (Jang et al. 2006; Zhuang et al. 2009). Natural (e.g., weathering, parent rock erosion, atmospheric deposition, and volcanic activities) and anthropogenic (e.g., sewage irrigation, manure addition, and use of fertilizers) activities are the general causes of soil and grain heavy metal contamination (Shah et al. 2012; Sekomo et al. 2011). Bolan et al. (2003) confirmed that the long-term application of biogas slurry leads to heavy metal accumulation in soils and grains. Heavy metals are not generally removed, even after the anaerobic digestion process. Excessive heavy metal accumulation in agricultural soils that results in elevated heavy metal uptake through food has elicited a significant amount of concern because of its potential health risks to local inhabitants (Pruvot et al. 2006). Atmospheric particulates are one of the most important air contaminants in China (Hu et al. 2010). Residents easily come into contact with airborne metals in atmospheric particulates through the fallout of particulates onto their food and drinks, inhalation of fine

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particulates, and dermal contact with particulate fallout during outdoor activities. Additionally, higher concentrations of potentially toxic metals have been reported in air particulates than in soil (Fang et al. 2010), and the integrated health risks of multi-elemental exposure through the inhalation of PM 2.5 are beyond acceptable levels (Diaz and Dominguez 2009). Given their non-biodegradable and persistent nature, heavy metals accumulate in soils and atmospheric particulates are assimilated by vegetables and water and accumulate in vital human organs such as the kidney, bone, and liver; they are associated with many serious health disorders (Duruibe et al. 2007).

Heavy metal intake by human populations through the food chain has been widely reported (Muchuweti et al. 2006). These metals may even enter the food chain posing an important risk to human health. Health risks due to the reuse of these biogas slurries as agricultural fertilizers were determined by local famers. In order to perform risk assessment of heavy metals in plants, a good understanding that the transfer characteristics of the heavy metals in soil-plant system should always be investigated is necessary (Lopes et al. 2012; Li et al. 2010). A multi-compartment fate and exposure model was used. This was the basis of a decision support tool for organic waste management (Río et al. 2011), to evaluate the transfer of heavy metals into the food chain and the possible impacts on human health, especially model parameterization related to plant and soil properties (Lopes et al. 2011). The mechanistic models are difficult to determine like diffusion coefficients of ions in the soil solution, root geometry and size, and kinetic parameters for the uptake of ions by the roots. For the purpose of risk assessment, these approaches may be too sophisticated and for this reason, environmental risk assessment methodology is applied to estimate the fate and exposure of several pollutants in the environment (Río et al. 2011). Environmental risk assessment process is constituted by four main steps: hazard identification, dose–response assessment, exposure assessment, and risk characterization (National Research Council 1993). Estimated daily metal intake rates are obtained from various media, including soil, drinking water, ambient air, and food (Nadal et al. 2005). Heavy metals can enter the human body through dermal contact, inhalation, and ingestion exposure from environmental media. Human health risk evaluations of heavy metals through various exposure pathways have been conducted (Baastrup et al. 2008; Man et al. 2010; Mari et al. 2009). The hazard quotient (HQ), formalized by the US Environmental Protection Agency (USEPA 2000), has been widely utilized to evaluate potential health risks associated with long-term exposure to metals in various media. This value is almost similar to the ratio between estimated daily intake (EDI) and oral reference dose (RfD) (Chien et al. 2002). Serious systemic health problems can develop as a result of excessive dietary accumulation of heavy metals in the human body (Oliver 1997). Although Zn

and Cu are essential elements, their excessive concentration in food and feed plants is hazardous because of their toxicity to humans and animals (Kabata-Pendias and Mukherjee 2007). Pb and Cd are considered potential carcinogens related to the etiology of several diseases, particularly cardiovascular, kidney, nervous system, blood, and bone diseases (Jarup 2003). A study has shown that soil and vegetables polluted by Pb and Cd in Copsa Mica and Baia Mare, Romania, significantly contribute to reduced human life expectancy in the affected areas; the average age is reduced by 9 to 10 years (Lacatusu et al. 1996). Dietary intake is a major exposure method for most people, although inhalation also plays an important role in highly contaminated sites (Tripathi et al. 1997).

With the rapid population explosion, industrialization, urbanization, and other human activities in the Taihu Basin, heavy metals in soils are becoming an increasingly serious environmental problem. Currently, a new mode of manure treatment is widely employed in the Taihu Basin. First, manure is collected uniformly from scattered and different-scaled pig farms and digested anaerobically with straw. The digested slurry is then applied to farmlands. In particular, vegetable fields are located near villages and conveniently close to farmers. However, this scenario means that the vegetables grown in these areas having soils irrigated with biogas slurry might be contaminated with metals and could cause potential health damage among residents. Human health risk evaluations of heavy metals through various exposure pathways have been conducted, but different media and systematic multi-pathway risk analyses are lacking. Therefore, studying the contaminant levels of environmental media in vegetables, grains, and related soils and assessing the potential health risks posed by heavy metal exposure to multiple media in such critical areas are necessary. Vegetables, grains, and related soils in areas irrigated with biogas slurry, which might be under risk, were selected in this study to investigate the contamination levels of soil, water, and grains and estimate the carcinogenic and non-carcinogenic risks to adults (i.e., farmers). The objectives of this study are as follows: (1) quantify the concentration of six metals in water, food, air, and soil in Taihu Basin, China; (2) estimate the daily intake (DI) of metals and the contribution of each medium; and (3) estimate the carcinogenic and non-carcinogenic risks posed to adults' (farmers) by heavy metal exposure to each medium. Chinese health risk assessment guidelines were adopted.

Materials and methods

Study area

The study area is located in the Taihu Basin and spans over 330 km^2. The area has a subtropical climate with an average annual temperature between 14.9 and 16.2 °C. Approximately

74 pig farms of different scales, which breed 1.5×10^4 pigs, are located in the study area. Most of these farms are small in scale. Approximately 63 pig farms, which account for 85 % of the total number of farms, have less than 500 pigs. However, the amount of feces produced by these farms is 42.516 t/day, which accounts for 48.6 % of the daily total manure generation.

Pig manure slurry was collected from farms of different scales and with different pig developmental stages (Fig. 1). After collection, the manure was mixed with straw for anaerobic digestion. The slurry was mixed in an adjusting tank and then pumped into a 1500 m³ continuous stirred tank reactor for anaerobic digestion. Biogas slurry and residues were utilized for soil amendment instead of chemical fertilizers. Food mainly included wheat, rice, and vegetables.

Sampling and pre-treatment

A total of 106 samples of soils amended with biogas slurry were collected from May 2013 to October 2013. The soils were randomly sampled at each site from the upper horizon (0 to 20 cm) and bulked together to form a composite sample. The samples were stored in sealed Kraft packages to avoid contamination. The soils were then air dried at room temperature (20 to 23 °C) before removing the unwanted materials, such as stones and other debris. The samples were then ground in an agate grinder and sieved through a 0.149 mm mesh to analyze the physico-chemical properties. Soil samples were digested with an HCl-HNO₃-HF-HClO₄ solution for the metal concentrations. First, approximately 0.5 g of a soil sample was weighed and digested with 10 mL of HCl on an electric hot plate at approximately 100 to 200 °C until the solution was reduced to 3 mL. Approximately 5 mL of HF, 5 mL of HNO₃, and 3 mL of HClO₄ were then added until no black material was found. The digestion continued with 3 mL of HNO₃, 3 mL of HF, and 1 mL of HClO₄ until the solution was completely clear. Finally, the digestion solution was transferred to a flask, and water was added to reach a fixed volume for further metal determination.

A total of 58 samples of amaranth, kalimeris, garlic, scallion, water spinach, greens, caraway, wheat, leek, Chinese cabbage, and rice were collected in 2013. The samples were collected by means of a completely randomized design. The food samples were washed with tap water to remove attached soil particles and rinsed twice with deionized water. The samples were then dried in an oven at 70 °C to a constant weight before being ground in an agate grinder and sieved through a 0.149 mm mesh. The food samples were analyzed through the procedure provided by Wang et al. (2003). First, approximately 0.5 g of plant samples were weighed and digested with 10 mL of HNO₃ and 1 mL of HClO₄. HNO₃ was added when the solution had dried up during the digestion process until no plant tissues could be detected in the digestion tube.
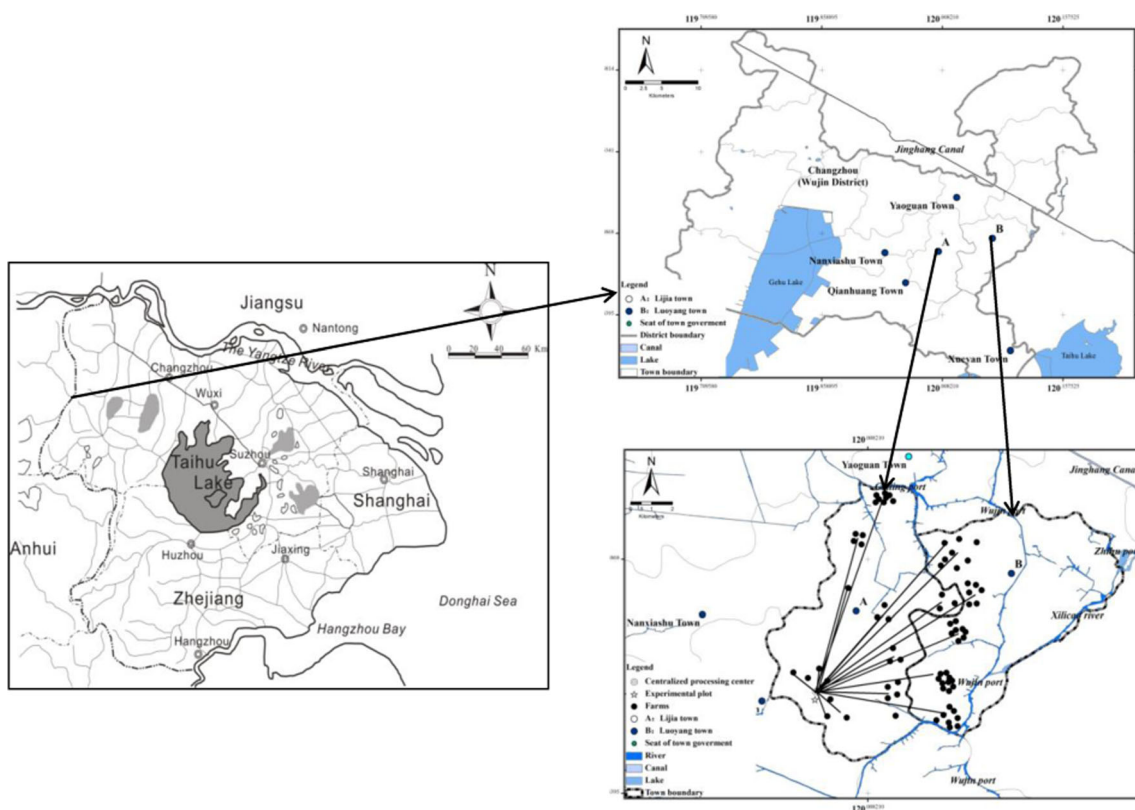

Fig. 1 A study area map showing the locations in Taihu Lake Basin

Atmospheric particulates (PM 2.5) were collected from two sampling sites in Changzhou. A total of 52 samples of PM 2.5 were collected monthly with membrane filters (20 cm^2 × 25 cm^2) by using an air sampler with a large volume (HY-1000, Qingdao Henyuan Instruments Co. Ltd., Qingdao, China) and a flow rate of 1.05 m^3 min^{-1}. A Milestone ETHOS 1 microwave sample preparation system (Milestone, Italy) with temperature control was utilized to digest the samples for the measurement of the total metals. Approximately 1/16 of a PTFE filter was utilized for PM 2.5, cut into fragments, and then digested in 6 ml of 65 % HNO$_3$ and 2 ml of 30 % H$_2$O$_2$ through the following two-stage digestion program: heating to 200 °C for 10 min (Stage 1) and incubation at 200 °C for 15 min (Stage 2). After cooling, the digested sample solutions were evaporated to near dryness, dissolved in 0.5 mL of 65 % HNO$_3$, and then diluted to 10 ml with Milli Q (MQ) water in a 10 ml flask (Hu et al. 2012). The solutions were subsequently stored in 25-ml high-density polyethylene vials at 4 °C until instrumental analysis. Precision and accuracy were verified through the use of standard reference materials available at the National Research Center for Geoanalysis, People's Republic of China (GBW07405, Soil). Blanks for digestion and the samples were prepared in duplicate. MQ water was utilized for dilution and dissolution.

Water used as drinking water was sampled from the farmland areas in the studied area. A total of nine samples were collected in 1 L acid-washed polyethylene bottles from local families at random to represent the entire area. After adding two drops of 65 % concentrated HNO$_3$ into the water samples, they were stored at −20 °C until analysis. Finally, the metal concentrations (i.e., Cu, Zn, Pb, As, Cd, and Cr) in the water samples were measured through inductively coupled plasma-mass spectrometry.

Samples analysis and quality assurance

Heavy metal concentrations were determined with an inductively coupled plasma optical emission spectrometer (Optima 5300, Perkin-Elmer SCIEX, USA) and an inductively coupled plasma-mass spectrometer (ICP-MS) (Agilent Technologies 7700 Series). The blank reagent, standard reference soil, and plant materials (GBW07603, GBW10010, and GBW07306 supplied by the National Research Center for Standards in China) were included in each sample batch to verify the accuracy and precision of the digestion procedure.

Data analysis

Enrichment factor

The pollution levels of Zn, Pb, Cu, Cr, As, and Cd in the samples were evaluated using the enrichment factor (EF), which is widely utilized to assess the pollution levels of metals. EF, which is a measure of the extent to which trace elements are enriched or reduced relative to a specific source, can be employed to differentiate metals that originate from human activities and those from natural provenance as well as assess the degree of anthropogenic influence (Meza-Figueroa et al. 2007). EF is calculated as follows:

$$EF = \frac{[C_x/C_{ref}]_{sample}}{[C_x/C_{ref}]_{background}}, \qquad (1)$$

where C_x is the concentration of the metal and C_{ref} is the concentration of the reference metal. C_{Fe} is the concentration of the reference element (Fe) in the studied samples or the continental crust. EF can assist in differentiating an anthropogenic source from natural ones. The degree of metal pollution can be classified into five categories: EF<2 (minimal), EF=2–5 (moderate), EF=5–20 (significant), EF=20–40 (very high), and EF>40 (extremely high). The degree of metals in PM 2.5 can be classified into two categories, namely, EF<10 (natural source) and EF>10 (anthropogenic source). EF can also assist in determining the degree of metal contamination.

Daily intake of heavy metals

The daily intake (DI) of heavy metals corresponds to the metal concentration in food crops. DI of metals for adults was determined with the following equation:

$$DI = C_{metal} \times W_{food}, \qquad (2)$$

where C_{metal} (mg kg^{-1}) is the heavy metal concentration in contaminated crops and W_{food} represents the daily average consumption of vegetables and grains in this region. The average body weight is 62.48 kg according to the survey of Yang et al. (2012). The C_{metal} of rice was converted with a factor of 0.86 because home-stored rice commonly contains 14 % water content (Zhuang et al. 2009). The metal intakes were compared with the tolerable DIs for metals recommended by the World Health Organization (1993) and the Food and Nutrition Board (2004).

Risk assessment methods

Human health risk models, including the carcinogenic and non-carcinogenic ones presented by USEPA, have been proven successful and are now adopted worldwide. Humans can be exposed to heavy metals from a medium through the main pathways listed in Table 1 (USEPA 2004, 2011; Ministry of Environmental Protection, People's Republic of China, 2014). The three exposure pathways are direct ingestion, inhalation through the mouth and nose, and dermal absorption of metals that adhere to exposed skin. The average daily dose (ADD)

Table 1 Defining equations of daily intake via various exposure pathway

Medium	Sources of heavy metals	Exposure pathway	Calculation formula
Soil	Heavy metals in soils	Ingestion	$ADD_{ing\text{-}soil}$
		Inhalation	$ADD_{inh\text{-}soil}$
		Dermal contact	$ADD_{derm\text{-}soil}$
Water	Heavy metals in water	Ingestion	$ADD_{ing\text{-}water}$
		Dermal contact	$ADD_{derm\text{-}water}$
Air (PM 2.5)	Heavy metals in dust	Inhalation	$ADD_{inh\text{-}air}$
		Dermal contact	$ADD_{derm\text{-}air}$
Vegetable (main and complementary)	Heavy metals in vegetables	Ingestion	$ADD_{ing\text{-}vegetable}$
Main food (wheat and rice)	Heavy metals in crops	Ingestion	$ADD_{ing\text{-}food}$

(mg kg^{-1} day^{-1}) of an element through ingestion, inhalation, and dermal contact exposure pathways can be estimated with Eqs. (3), (4), and (5), respectively.

$$ADD_{ing} = \frac{C \times IngR \times EF \times ED}{BW \times AT}, \tag{3}$$

$$ADD_{inh} = \frac{C \times InhR \times EF \times ED}{PEF \times BW \times AT}, \tag{4}$$

$$ADD_{derm} = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT}, \tag{5}$$

where C is the metal concentration in milligrams per kilogram in the medium, IngR is the ingestion rate in milligrams per day, InhR is the inhalation rate in cubic meter day, PEF is the inhalation factor for respirable particles in cubic meters per kilogram, SA is the surface area of the skin exposed to pollutants in square centimeters, AF is the skin adherence factor in milligrams per square centimeter hour, ABS is the dermal absorption factor, EF is the exposure frequency in days per year, ED is the exposure duration in years, BW is the body weight in kilograms, and AT is the average time in days.

Carcinogenic and non-carcinogenic risk assessments for all the metals entering through ingestion, inhalation, dermal, and diet exposure pathways were conducted. The non-carcinogenic risk from individual heavy metals can be expressed as HQ by using Eq. (6).

$$HQ = \frac{ADD}{RfD}, \tag{6}$$

where RfD is the estimated maximum permissible risk imposed on humans through daily exposure. The three thresholds are RfD (mg kg^{-1} day^{-1}) for ingestion, RfD (mg kg^{-1} day^{-1}) for

dermal contact, and RfD (mg m^{-3}) for inhalation. Experiencing adverse health effects is unlikely when HQ≤1, whereas potential non-carcinogenic effects can occur when HQ>1 (Al-Saleh et al. 1999).

Moreover, the HQ calculated for each metal is summarized to assess the overall potential non-carcinogenic effects posed by more than one heavy metal (e.g., i). If multiple pathways are available, a total exposure hazard index (HIt) can be utilized to communicate non-cancer risks through different pathways; this index can be expressed as Eqs. (7) and (8) as follows (USEPA 2011):

$$HI = \sum_1^n HQ, \tag{7}$$

$$HIt = \sum_1^n HI. \tag{8}$$

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

Cancer risk (CR) and total CR (TCR) can be evaluated as follows:

$$CR = ADD \times SF \tag{9}$$

$$TCR = \sum_1^k CR, \tag{10}$$

where ADD is the chronic DI (mg kg^{-1} day^{-1}) and SF is the slope factor (kg day^{-1} mg^{-1}). The acceptable or tolerable risk for regulatory purposes is within the range of 10^{-6} to 10^{-4} (USEPA 2001).

The body weights of adults were obtained through a questionnaire-based exposure survey to calculate the ADD of each pathway. Other exposure parameters, such as IngRs

and SA, were obtained from literature (Gržtić 2008; Lai et al. 2010). The doses calculated for each metal and exposure pathway were subsequently divided by the corresponding reference dose (RfD) (mg kg^{-1} day^{-1}) to yield an HQ (non-cancer risk), whereas the dose for carcinogens was multiplied by the corresponding SF (mg kg^{-1} day^{-1}) to produce a cancer risk level. In accordance with the classification group orders defined by the International Agency for Research on Cancer, Pb, Zn, Cu, Mn, Cr, and Cd were regarded as non-cancer effect elements, whereas Cr, Cd, As, Ni, and Co were treated as having a potential carcinogen effect. The SF, RfD, and RfC (i.e., gastrointestinal absorption factor used to calculate dermal SF) were based on the technical guidelines for risk assessment of contaminated sites (Ministry of Environmental Protection, People's Republic of China 2014).

Statistical analysis

The data were statistically analyzed with the Statistical Package for the Social Sciences (SPSS, version 19.0) and Microsoft Excel (2010) to accommodate the uncertainties associated with the calculation process and exposure factors. The measurements were expressed in terms of mean and standard deviation.

Results and discussion

Heavy metal concentrations in soils irrigated with biogas slurry

The heavy metal concentrations in the soils are presented in Fig. 2a. Unlike the Chinese Soil Environmental Quality Standard (GB15618-2008), the mean concentrations of Zn, Cd, and Pb in the soils exceeded the upper limits of the Chinese Soil Environmental Quality Standard II. The mean concentrations of Cr and Cu were below the standard. Notably, the concentrations of As in the soils were almost similar to the given value in the standard. The heavy metal concentrations in the soils were much higher than those in other studies (Cai et al. 2012). The contamination degrees of Zn, Pb, and Cd were severe in the study area. Moreover, heavy metal contaminations varied in wide ranges in the soil samples across the area and were in the order of Zn>Pb>Cu>Cr>As>Cd. The heavy metal concentrations differed among soils of different vegetables and grains because of the different accumulation capabilities of the metals and various soil properties. The majority of vegetable soils contained high concentrations of heavy metals.

The concentrations of six metals in coriander soil were the lowest and much lower than the background value. This condition is due to leafy vegetables having high translocation and high transpiration rates unlike other vegetables. The transfer of heavy metals from root to stem and further into the vegetable is also longer, which results in lower accumulation than in leafy vegetables (Muchuweti et al. 2006). This result is consistent with the finding that leafy vegetables accumulate higher heavy metal concentrations in their edible parts than root and fruit vegetables in Cd-contaminated soils (Yang et al. 2009). The mean metal concentrations in wheat soils were much higher than in rice soils. The above results clearly show that plants (i.e., vegetables and grains) grown on contaminated soils accumulate higher levels of metals in their edible parts compared with those grown on less contaminated soils.

The EF values of metals were calculated for each soil sample relative to the background value of the elements in the local soil (China National Environmental Monitoring Center 1990). All mean EF values for all metals decreased in the order of 20>Cd=18>Zn=6>5>Pb>Cu>2>Cr>As>0 (Fig. 2c). This result indicates that the soils were contaminated by metals derived from anthropogenic sources. The mean EF values for Pb and Cu in soils fell under the category of moderate contamination, whereas the mean EF values for Cr and As fell under the category of minimal contamination according to the ranking criteria (five categories). The mean EF values of Zn and Cd in all the samples in 5–20 revealed that soils were significant pollutants. EF also played an important role in assessing the contamination levels of soils. These results imply that vegetable and grain soils irrigated with biogas slurry should receive more attention because they are highly contaminated with heavy metals.

Heavy metal concentrations in vegetables and grains in related soils irrigated with biogas slurry

Among the vegetables, amaranth, *Kalimeris indica* (referred to as kalimeris hereon), water spinach, greens, leek, and Chinese cabbage are the main vegetables (MV). Garlic, scallion, and coriander are the complementary vegetables (CV). Rice is the major grain; the low amount of flour products made from wheat reflects the eating habits of people in the Taihu Basin. The heavy metal concentrations in rice, wheat, MV, and CV are presented in Fig. 2b. A relatively large variation in heavy metal concentrations can be clearly observed among all of the food. The vegetable samples collected in summer had relatively higher heavy metal concentrations than those collected in autumn. Kalimeris showed the highest mean concentration of Cu among the vegetables (1.74 mg kg^{-1}). The highest Zn, Pb, As, Cd, and Cr concentrations were observed in garlic (18.12 mg kg^{-1}), water spinach (1.28 mg kg^{-1}), amaranth (0.56 mg kg^{-1}), water spinach (0.52 mg kg^{-1}), and garlic (0.78 mg kg^{-1}), respectively. The mean Cu and Pb concentrations in rice were higher than those in wheat. The Cu concentration in rice was 6.70 mg kg^{-1} (on a dry weight basis), which was far higher than that in wheat (2.76 mg kg^{-1}). The other heavy metal concentrations are comparable.
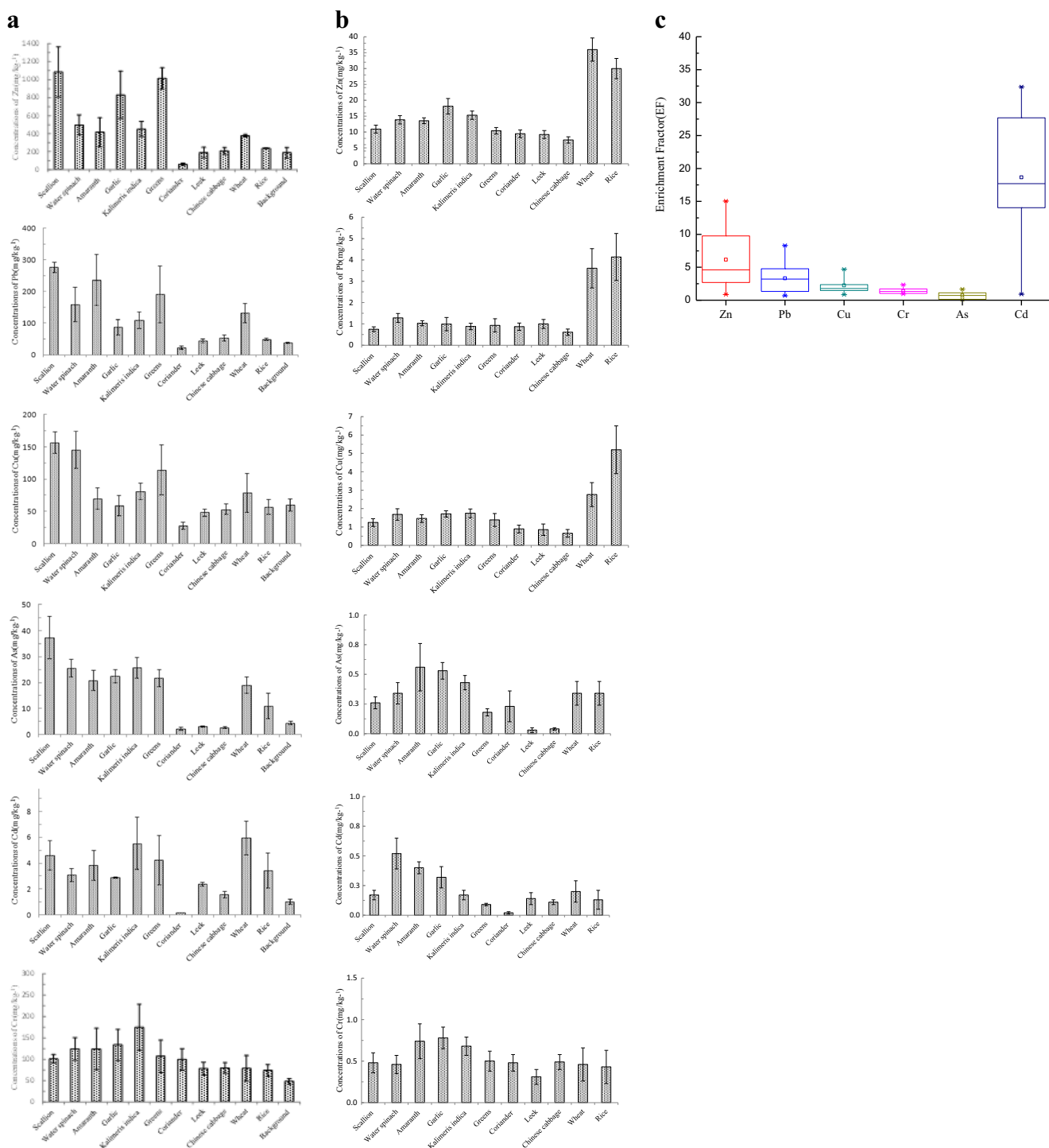
Fig. 2 Concentration and enrichment factor of heavy metals in soils-vegetables-grains. **a** concentration of heavy metals in soils, **b** concentration of heavy metals in vegetables and grains, **c** enrichment factor of heavy metals in soils

The mean concentrations of Cu, Zn, Pb, As, Cd, and Cr were compared with the maximum permissible amount of contaminants in food (Chinese National Standard: GB18406.1-2001 for Pb, As, Cd, and Cr; GB15199-1994 for Cu; and GB13106-1991 for Zn) recommended by the Ministry of Health of the People's Republic of China. The

Zn, Pb, and Cd concentrations in grains exceeded the upper limits of these standards. The Zn, Pb, and Cd concentrations in rice grown in this area were 1.8, 20.7, and 2.6-fold larger than the maximum permissible levels, respectively (i.e., 20, 0.2, and 0.05 mg kg^{-1}, respectively). The Pb concentration of rice is much higher than that in the Chenzhou Pb/Zn mining area

of Southern China (Liu et al. 2005). The Cd concentration of rice was 0.11 mg kg^{-1} to 0.25 mg kg^{-1}; although this value is much lower than that around Dabaoshan mine in Southern China (Zhuang et al. 2009), it exceeds the upper limit of the standard. Reeves and Chaney (2001) suggested that Cd is of primary concern in soil and food contamination, particularly in rice systems. In the study area, approximately 1.09 mg kg^{-1} to 4.20 mg kg^{-1} of Cu, 33.95 mg kg^{-1} to 43.84 mg kg^{-1} of Zn, 2.43 mg kg^{-1} to 5.42 mg kg^{-1} of Pb, 0.19 mg kg^{-1} to 1.78 mg kg^{-1} of As, 0.13 mg kg^{-1} to 0.39 mg kg^{-1} of Cd, and 0.43 mg kg^{-1} to 0.65 mg kg^{-1} of Cr were accumulated in wheat. Huang et al. (2008) reported that the Pb, As, Cd, and Cr concentrations in wheat grain are 0.177, 0.038, 0.055, and 0.108 mg kg^{-1}, respectively, which are much lower than those in the present study. The mean concentrations of Cr were 0.43 and 0.46 mg kg^{-1} in rice and wheat, respectively, which are near the upper limits (0.5 mg kg^{-1}).

The Pb and Cd concentrations in vegetables exceeded the highest limits, whereas the Cu, Zn, As, and Cr concentrations fell within the permitted range. The mean concentrations of Cr in amaranth and kalimeris were 0.74 and 0.68 mg kg^{-1}, respectively, and exceeded the upper limits (0.5 mg kg^{-1}). The Cr concentrations in several water samples of spinach and greens also exceeded the upper limits. Compared with those in previous relevant reports on vegetables and grains (Santos et al. 2004; Zheng et al. 2007), the heavy metal concentrations in the present study are higher. Zhou et al. (2005) showed that a positive correlation exists between heavy metal concentrations in soils and those in plants. Zn absorption was found to be the fastest in the selected vegetables, consistent with Zheng's report (2007). The vegetables were clearly heavily polluted by Pb and Cd. Previous studies confirmed that leafy vegetables, such as amaranth, can accumulate high Pb and Cd concentrations in their edible parts; this condition suggests that the mobility of Pb and Cd in soils relies on the crop's physiological features (Wang et al. 2006).

Heavy metal concentrations in PM 2.5 and water

The concentrations of elements (i.e., Zn, Pb, Cu, As, Cd, and Cr) in PM 2.5 were analyzed (Fig. 3a). The Zn and Pb concentrations in PM 2.5 were much higher than those of other heavy metals, suggesting that these metals are the major metals of these fractions (Hu et al. 2012). The average heavy metal concentrations in PM 2.5 were in the order of Zn>Pb> Cu>Cr>As>Cd. These findings are similar to those on metallic element concentrations, which occur in the order of Fe> Zn>Pb≈Cu>Cr>As>Cd. The average As and Cd concentrations in PM 2.5 in Shanghai are higher than those in the present study, whereas the Cu concentration in this study is higher than that in Shanghai (Chen et al. 2008). The Pb, Cu, Zn, and Cr concentrations in PM 2.5 in the present study were all in the median range of their concentration values in PM 2.5 for

Asian countries (Fang et al. 2010). The aerosol-crust EFs were calculated to distinguish the anthropogenic inputs to atmospheric metals (Fig. 3b). According to conventional classification criteria, an EF value larger than 10 indicates the anthropogenic origin of an element that comprises a significant proportion of the total elements (Chen et al. 2008). The average EF values were below 10 for Cd and Cr, which suggests that these elements were mainly from natural sources. The average EF values for As, Cu, Pb, and Zn were above 10, which suggests that these elements were obtained from anthropogenic sources. Moreover, high enrichment of Cu, Zn, As, Cd, and Pb in PM 2.5 in Shanghai was observed (Chen et al. 2008). These findings collectively indicate that Cu, Zn, As, and Pb are the main anthropogenic toxic elements in atmospheric particulates in the Taihu Basin.

The drinking water in the studied area is safe because all heavy metal concentrations were lower than the standards for drinking water quality (GB5749-2006). The mean concentrations of Cr, As, Cd, Cu, Pb, and Zn in water were 3.14, 0.22, 0.30, 1.32, 3.75, and 96.36 μg/L, respectively, which are lower than the limiting values defined in the standards. This water type is also used for drinking. Thus, the water sources represent drinking water for all participants in the discussion below.

DI of metals and target HQs

Human exposure to heavy metals mainly occurs through the routes of inhaled aerosol particles, soil, food, and water, and the main pathways for adults include aerosol inhalation, hand-to-mouth activities, and dermal contact (Diaz-Somoano et al. 2009). The DIs of heavy metals for adults in the Taihu Basin through food consumption are presented in Table 2. People commonly consume different food types. CVs generally comprise 5 % of the total vegetable consumption. A survey in the Taihu Basin showed that adults consume 380.93 g of rice, 21.33 g of wheat, 266.53 g of MV, and 14.03 g of CVs (Yang et al. 2013). The DI of heavy metals was evaluated according to the average concentration of each heavy metal in each type of food and corresponding consumption rate (Santos et al. 2004). The DIs for heavy metals in food are in the following order: Zn>Cu>Pb>Cr>As>Cd; intake from grains was larger than that from vegetables for all metals except Cd. The highest DIs of Pb (1941.76 μg day^{-1}), As (242.82 μg day^{-}), and Cd (136.13 μg day^{-}) for adults through food consumption were considerably higher than the provisional tolerable DI values by 8.7, 1.8, and 2.2 times, respectively. The recommended daily DIs of Cu and Zn for adults are 6.5 mg and 33 mg, respectively (Raghunath et al. 1999). The largest contribution of the intake of Cu, Zn, Pb, and As originated from rice. Vegetables contributed the most Cd and Cr in DI. Thus, the perennial intake of these contaminated food can likely induce adverse health effects largely from Pb, As, and Cd exposure. The DIs of heavy metals (i.e., Cu, Zn, and Pb) through cereal and vegetable

Fig. 3 **a** Average (*square*), median (*central horizontal bar*), 25th and 75th percentiles (*lower and upper base*), 1st and 99th percentiles (*lower and upper asterisks*), and minimum maximum) concentrations of heavy metals in PM 2.5 samples collected from the study area. **b** Average EF values of heavy metals in PM 2.5 samples collected from the study area. *Error bars* represent the standard deviation
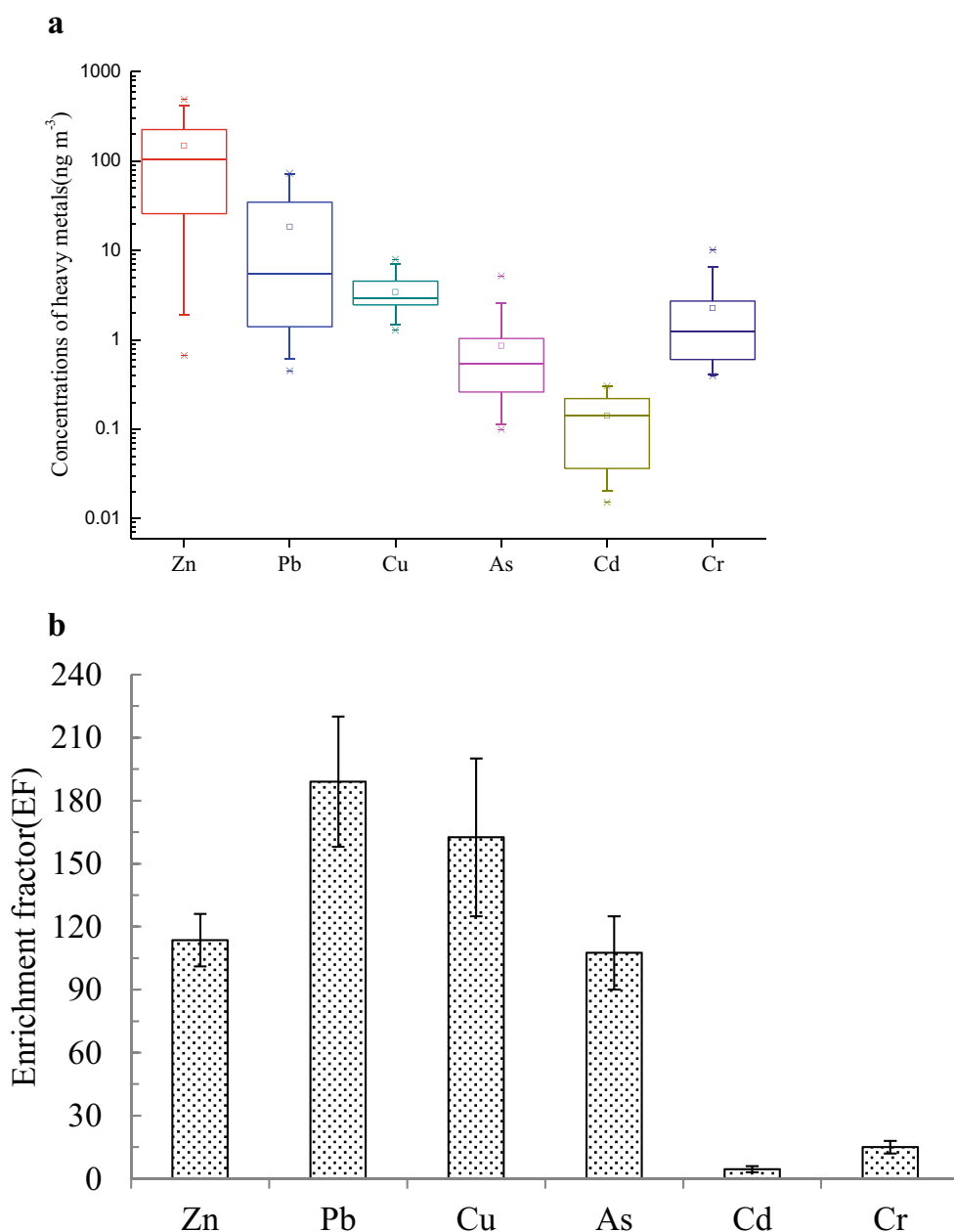
consumption by local inhabitants in the study area were higher than those in the vicinity of the Dabaoshan mine located in Southwest China (Zhuang et al. 2009); however, the DI of Cd was lower. Lee et al. (2006) found that the DIs of Pb and Cd for adults are 24.4 and 14.3 μg day⁻, respectively, which are smaller than the values in the present study. People are suffering from Pb, As, and Cd contamination through grain and vegetable consumption in the study area.

Table 2 Dietary intake of heavy metals (μg day⁻) via consumption of rice, wheat, and vegetables

Type of food	Daily Intake (g day⁻)	Cu	Zn	Pb	As	Cd	Cr
MV[a]	266.53	418.46	3534.21	274.53	101.28	79.96	167.92
CV[b]	14.03	17.96	179.98	13.19	4.77	2.38	8.00
Rice	380.93	2552.24	13,934.48	1577.06	129.52	49.52	163.80
Wheat	21.33	58.86	892.99	76.99	7.25	4.27	9.81
Total		3047.52	18,541.66	1941.76	242.82	136.13	349.52

[a] *MV* main vegetables
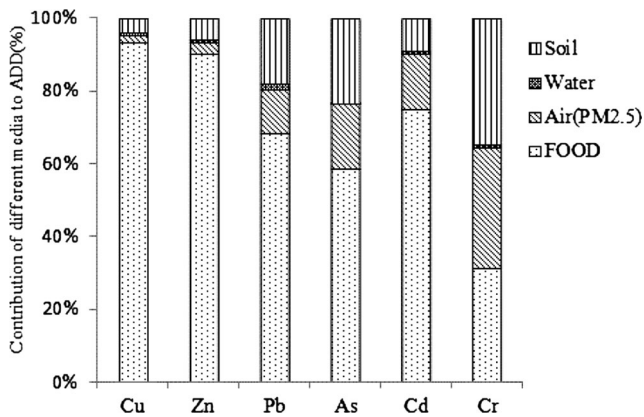
[b] *CV* complementary vegetables

Fig. 4 The contribution of air (PM 2.5), water, soil, and food via inhalation, ingestion, and dermal contact to the average daily exposure dose

Based on the heavy metal contents in each environmental medium and the intake rates of air, water, food, and soil by adults obtained from the questionnaires, the daily exposure doses of heavy metals and metalloids for adults were evaluated. The contribution of each exposure route to the adults' ADD is shown in Fig. 4. Food ingestion plays an important role in the total ADD of most metals, especially for Cu and Zn, which account for 94 and 91 %, respectively. By contrast, water and air ingestion contribute less than 5 %. For Cr, the inhalation pathway through air (32 %) contributed nearly as much as the ingestion pathway through food (31 %) and the three pathways through soil (34 %). In addition, the intakes of Cd, Pb, and As in staple food accounted for majority of the total ADD, which implies that staple food can pose a high risk to local adults through the ingestion pathway. Interestingly, soil ingestion was the second most important factor for daily As and Pb intake, which accounted for 18 and 22 % in the

study area, respectively. Rice intake was the major source of Cd exposure, which accounted for 62 % of the total DI estimate in the study area. Rice intake also constituted a major portion of the DI of Cu, As, Pb, Cd, and Zn in both populations. The substantial contribution of rice and soil to the intake of the five heavy metals indicates that the contamination of soil and rice by metal should receive more attention, especially in the areas irrigated with biogas slurry in the Taihu Basin.

Health risk assessment

Non-carcinogenic risk assessment of heavy metals in different exposures

Based on the ADD and RfD of each pollutant, the non-cancer risks posed by heavy metals from different media to local adults are shown in Table 3. The HIt of heavy metals in adults decreased in the order of As>Pb>Cd>Cr>Cu>Zn. With regard to the pathways, the highest non-carcinogenic risk was from food ingestion (17), followed by soil ingestion, air inhalation, air ingestion, and dermal contact with air. The risk of metals by food ingestion was the highest in rice (5.3), followed by MV (1.2), and wheat (0.26). In consideration of the two major elements (metal and pathway), the highest risk was observed for the ingestion of As-contaminated rice (5.8), followed by ingestion of Pb-contaminated rice (5.3) and ingestion of Cd-contaminated MV (0.79). Therefore, the ingestion exposure of these heavy metals largely contributed to the non-cancer effect. These results illustrate that the higher non-carcinogenic risks can also be explained by the fact that more toxic metals in the integrated exposure pathway being considered for the health effect in this study. The HIt of Pb and As was larger than 1,

Table 3 Non-carcinogenic risk of heavy metals for adults

Type	Pathway	HQ_{Cu}	HQ_{Zn}	HQ_{Pb}	HQ_{As}	HQ_{Cd}	HQ_{Cr}	Total
Soil	Ingestion	3.7E−02	4.9E−02	6.2E−01	1.1E+00	6.7E−02	6.3E−01	2.5E+00
	Inhalation	5.5E−06	7.2E−06	9.1E−05	5.8E−03	9.8E−06	9.7E−03	1.6E−02
	Dermal	4.2E−04	8.3E−04	1.4E−02	9.3E−03	2.2E−02	1.1E−01	1.5E−01
Water	Ingestion	7.9E−07	7.7E−09	6.4E−08	1.8E−08	1.4E−08	2.5E−08	9.2E−07
	Dermal	1.2E−13	6.1E−15	2.8E−16	1.9E−15	6.3E−14	1.1E−13	3.0E−13
Air (PM 2.5)	Ingestion	7.9E−03	2.3E−02	3.8E−01	1.7E−01	1.8E−02	9.3E−03	6.0E−01
	Inhalation	1.0E−02	–	–	5.3E−01	2.1E−01	2.2E−01	9.7E−01
	Dermal	1.8E−03	2.4E−03	4.0E−02	7.2E−02	7.9E−03	3.0E−01	4.2E−01
Food	Ingestion	9.9E−01	8.4E−01	6.8E+00	7.1E+00	1.6E+00	3.3E−03	1.7E+01
MV[a]		1.1E−01	1.7E−01	1.2E+00	6.0E−01	7.9E−01	1.6E−03	
CV[b]		1.0E−02	1.0E−02	7.0E−02	3.6E−01	5.0E−02	1.0E−03	
Rice		8.5E−01	6.2E−01	5.3E+00	5.8E+00	6.6E−01	1.5E−03	
Wheat		2.0E−02	4.0E−02	2.6E−01	3.3E−01	6.0E−02	1.0E−03	
	Hit	1.0E+00	9.1E−01	7.9E+00	9.0E+00	1.9E+00	1.3E+00	

[a] *MV* main vegetables

[b] *CV* complementary vegetables

Fig. 5 Multi-pathway analysis of HQ. **a** Each pathway's contribution to the total Pb exposure of the local adults; **b** Each pathway's contribution to the total As exposure of the local adults; *MV* the main vegetables; *CV* the complementary vegetables
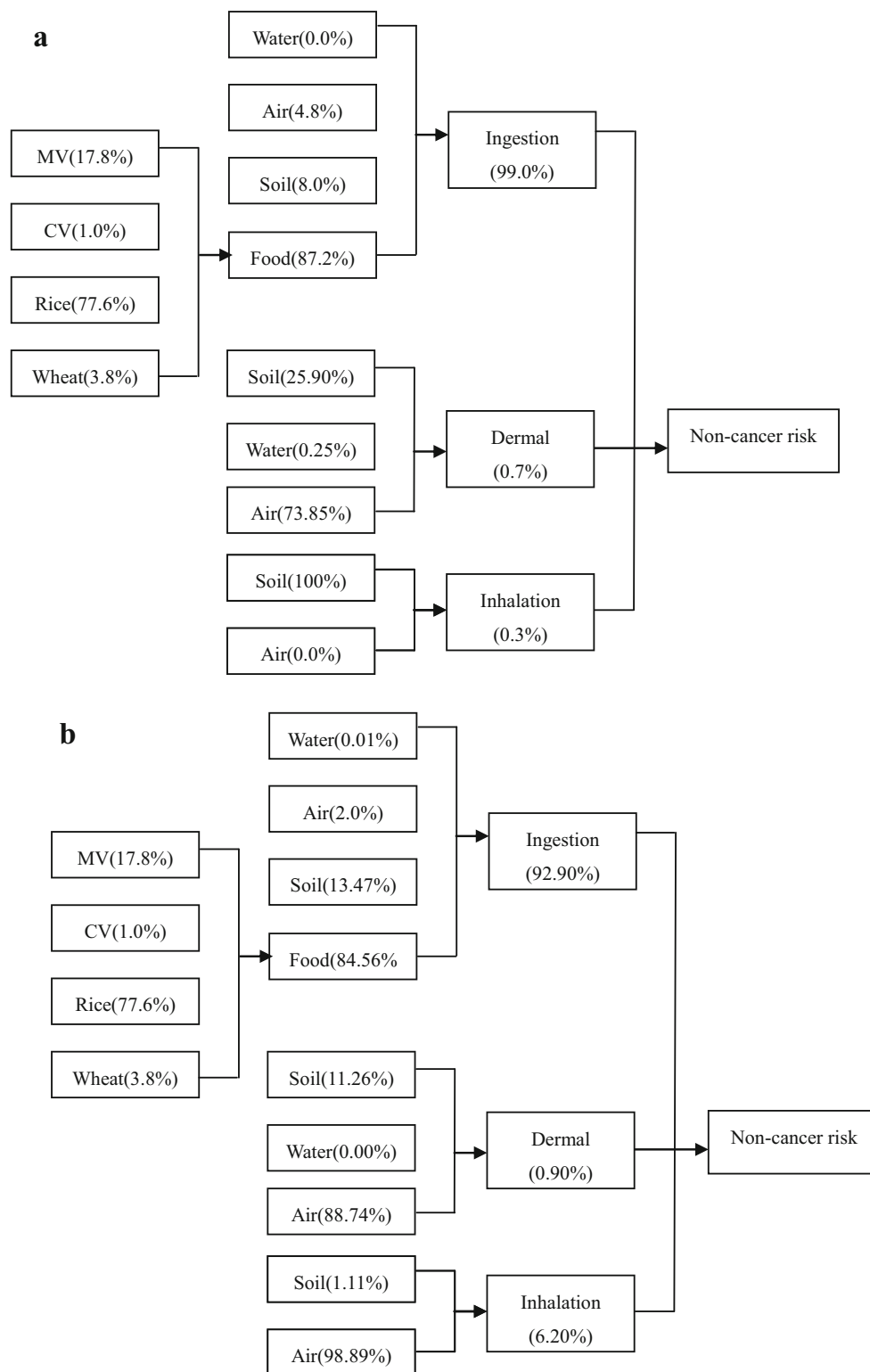
indicating that the DI of individual metals could be highly deleterious to the health of the local inhabitants. This condition also applies to Pb from rice consumption. The HIt of Zn was less than 1, indicating that the potential health risk of Zn is the lowest. This condition suggests that local inhabitants are not exposed to a potential health risk from dietary As and Pb. Wang et al. (2005) also found that the THQ of Cr in food consumption is minimal compared with those of Cu, Zn, Pb, and Cd. The results indicate that As, Pb, and Cd are the major components that contribute to the potential health risk, which is

consistent with a separate assessment for an area near a smelter in Nanning, China (Cui et al. 2004), and in the vicinity of smelters in Boolaroo, Australia (Kachenko and Singh 2006). The data produced in the present study clearly show that Pb, As, and Cd pose significant risks to local inhabitants through the consumption of contaminated rice, wheat, and vegetables. These results indicate that local adults (farmers) are exposed to a heavily polluted environment. The heavy metals in the environmental media can pose high health risks to local farmers through several exposure pathways because of certain intakes from each exposure medium.

The majority of non-cancer risks was contributed by Cr, Cu, Pb, Cd, As, and Zn through ingestion and exposure. With As and Pb as examples, each pathway's contribution to the total exposure of local farmers was calculated based on the average HQ values shown in Fig. 5. This figure shows that exposure to As and Pb is mainly from food ingestion; As and Pb exposures contributed 99 and 92.9 % to the total HQ, respectively. The CVs and wheat contributed nearly equally. Inhalation exposure and dermal contact with Pb contributed minimally (Fig. 5a). Local adults' exposure to As mainly occurred through food and soil ingestion and air (PM 2.5) inhalation (Fig. 5b). Air inhalation was the second primary pathway to As exposure, which contributed nearly 6.2 % to the total HQ.

Carcinogenic risk assessment of heavy metals in different exposures

Another important factor in assessing health risks is the cancer risk. The cancer risk posed to adults through heavy metal contamination in different exposures was determined, and the results are presented in Table 4. The table shows that the cancer

risk of Cr, As, and Cd was 7.98×10^{-2}, 3.79×10^{-3}, and 6.68×10^{-4}, respectively. These values exceed the health limit of 1.0×10^{-4}. The cancer risks decreased in the order of Cr, As, and Cd. Therefore, Cr is the main pollutant source that induces cancer. The carcinogenic risk through food and soil ingestion was mainly attributed to As and Cr, which had carcinogenic risk levels that are 32 times and even 100 times higher than the acceptable level of 1.0×10^{-4}. In addition, the carcinogenic risk through food ingestion mainly attributed to Cd can pose potential carcinogenic risks to adults because its risk levels are higher than the acceptable level. Considering ADD and metal contents, Cd and As from food ingestion as well as Cr from soil ingestion can pose a potentially high carcinogenic risk to local adults. Cancer risks exist in all soils exposed to Cr pollution, with a lifetime carcinogenic risk. The soil exposure medium of Cr is considered detrimental to adults through ingestion, inhalation, and dermal contact. The results of the present study reveal high carcinogenic risk levels (consistent with the results of a previous study) caused by the high Cr pollution in the soils irrigated with biogas slurry in the studied area.

These results imply that vegetable and grain soils irrigated with biogas slurry should receive more attention because of their high contamination by heavy metals.

Conclusions

This study presented an assessment of heavy metal contamination in air, water, vegetables, grains, and related soils irrigated with biogas slurry and determined the potential health risk encountered through different exposure pathways. Emphasis was placed on the effects of different media and exposure pathways. The following conclusions were drawn.

(1) Biogas slurry irrigation is the main cause of metal accumulation in food and related soils. Heavy metals (i.e., Cd, Zn, and Pb) in soils showed high EF. Furthermore, grown vegetables and grains were contaminated with Pb and Cd and exceeded the permissible limits for vegetables set by the Ministry of Health of the People's Republic of China. The findings indicate that Cu, Zn, As, and Pb are the main anthropogenic toxic elements in atmospheric particulates in the Taihu Basin.

(2) The DIs for heavy metals in food decreased in the following order: Zn>Cu>Pb>Cr>As>Cd; intake from cereals was more than that from vegetables for all metals except Cd. Food ingestion plays an important role in the total ADD for most metals, especially for Cu and Zn, which accounted for 94 and 91 %, respectively.

(3) The HIt of heavy metals in adults decreased in the order of As>Pb>Cd>Cr>Cu>Zn. The non-carcinogenic risks posed to adults mainly resulted from Cu, Zn, Pb, Cd, and As through food ingestion and from Cr through

Table 4 Carcinogenic risk of heavy metals for adults

Type	Pathway	As	Cd	Cr	Total
Soil	Ingestion	5.1E−04	2.5E−05	7.9E−02	7.95E−02
	Inhalation	1.7E−05	1.3E−06	2.7E−04	2.88E−04
	Dermal	1.7E−06	8.5E−08	2.7E−04	2.72E−04
Water	Ingestion	7.9E−06	4.4E−05	3.8E−05	8.99E−05
	Dermal	8.5E−13	1.2E−13	3.3E−12	4.27E−12
Air (PM 2.5)	Ingestion	3.4E−05	6.3E−06	5.1E−06	4.54E−05
	Inhalation	1.2E−05	1.5E−06	5.6E−05	6.95E−05
	Dermal	1.1E−05	2.6E−08	9.5E−05	1.06E−04
Food	Ingestion	3.2E−03	5.9E−04	4.2E−05	3.83E−03
MV[a]		2.7E−04	3.0E−04	2.0E−05	
CV[b]		1.6E−04	1.9E−05	1.3E−06	
Rice		2.6E−03	2.5E−04	1.9E−05	
Wheat		1.5E−04	2.3E−05	1.3E−06	
	Ilcr	3.79E−03	6.68E−04	7.98E−02	

[a] *MV* main vegetables

[b] *CV* complementary vegetables

soil ingestion. The highest non-carcinogenic risk was determined from food ingestion, followed by soil ingestion, air inhalation, air ingestion, and dermal contact with air.

(4) The integrated carcinogenic risks posed to adults decreased in the order of Cr, As, and Cd and mainly resulted from As and Cd through food ingestion and from Cr through soil ingestion. Both cancer and non-cancer risks through dermal contact can be ignored. Therefore, more attention should be paid to the health risks caused by adults' (farmers) exposure to heavy metals in soils irrigated with biogas slurry in Taihu Basin, China, so that effective measures can be implemented to address heavy metal pollution.

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