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Exposure risk assessment of nine metal elements in Chongqing hotpot seasoning

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Atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) were used to analyze the contents of nine metal elements (Pb, As, Hg, Cd, Cr, Fe, Mn, Cu, Zn) in 100 groups of Chongqing hotpot seasoning (CHS). Meanwhile, Crystal Ball software based on Monte Carlo simulation technology was used to assess the exposure risk of the nine metal elements in CHS for people of different ages in Chongqing. In general, the average Hazard Index (HI) of the nine metal elements is 0.306 < 1, indicating no non-carcinogenic risks from these nine elements for inhabitants of Chongqing under the current consumption level of CHS. Children (ages 7-13) and adult women have higher chronic daily intake (CDI) than adult males. The carcinogenic risk of Pb, As and Cd are within the acceptable risk level (10^{-6} to 10^{-4}). The sensitivity analysis suggests that the contents of the nine metal elements and daily intake (PIR) in CHS were positively correlated with the risk index, while the body weight was negatively correlated with the risk index. This study provides a scientific basis for guiding the safe consumption of Chongqing hotpot, and provides a theoretical basis for the development of safety-compliant CHS quality standards.

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1. Introduction

The pursuit of gourmet food is very important in Chinese cuisine culture. As a branch of Chinese cuisine culture, the Hotpot culture is becoming more and more popular in China, especially the spicy hotpot originating in Chongqing.¹ The production of Hotpot seasoning as the main source of hotpot flavor, with the increasing popularity of hotpot, has been industrialized. Chongqing hotpot seasoning (CHS) is cooked by boiling animal oil or vegetable oil with spicy foods (such as chilli, zanthoxylum, ginger, garlic) and other spices by fire. When eating, the hotpot seasoning is put into a metal pot and boiled with water to make the spicy, hot spicy and delicious taste spill over and dissolve in the soup, then cook the food materials.² Finally, cooked food is dipped in sauce and eaten. This whole process named as "Tang huoguo" in China.³

At present, CHS has been sold at home and abroad, and will be produced in the world in the future. Therefore, it is necessary to establish quality standards for safety-compliant CHS. The content analysis of metal elements in CHS, which may come from raw materials, productive process and use phase, is an important part of constructing standards and ensuring food safety. In China, the safe contents of metals such as Pb and As in CHS are determined according to the national food safety standards, 4 while other metals such as Hg, Cd, Cr, Mn, Cu, Zn and Fe have no relevant limit standards, and there is no relevant

research report on the content and exposure risk of metal elements in the CHS.

Metal elements, especially heavy metals, has the characteristics of toxicity, bioaccumulation and non-degradability.⁵ It has been confirmed that the main reason for the contamination of food by metal is man-made activities.⁶ Heavy metals accumulate in the soil, leading to the decrease of crop yield and quality.⁷ Eating contaminated crops will have a negative impact on humans, animals and ecosystems.⁸

The metal elements in CHS are mainly from the raw materials. At present, there are many reports about metal enrichment in food at home and abroad, but different food in different countries and regions are polluted by metals differently.9 Jafarian-Dehkordi A.10 detected vegetables (cucumbers, tomatoes, cabbage, lettuce, potatoes, onions, carrots, leeks, dill, spinach, cilantro, parsley) grown in the suburbs of Isfahan for Cd, Cr and Pb levels all above the WHO/FAO limit. Arora M.11 showed that vegetables irrigated with wastewater from different sources had large accumulation of Zn, Mn and Fe. Luo C.12 found that local soil and vegetables that dispose of e-waste carelessly were heavily polluted by metals (Cd, Cu, Pb, Zn). In China, the pepper cultivated in Yanqi basin of Xinjiang is heavily polluted with Pb and Zn, while slightly polluted with Cd and Cr.13 Chilies grown around the smelter in Guizhou are rich in Cd.14 There are different levels of Zn and As pollution in Lanzhou vegetable base.15 The pollution of Cu and Cr in Zanthoxylum base on the suburb of Weinan is serious, 16 and the Pb pollution of chile in Shaanxi exceeded 1 mg kg $^{-1}$. In general, it is of practical significance to carry out metal content detection in CHS.

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Exposure assessment is to calculate the data of pollutant exposure level survey from the perspective of human health, so as to directly evaluate the harm of pollutants to residents' health and establish an objective risk assessment model.18 There are two main risk assessment methods for chemical hazards in the world. One is a risk assessment method based on quantitative model,19 and the other is a risk assessment method based on uncertainty model (such as Monte Carlo method). Compared with the two methods, the method based on the uncertainty model is more intuitively and more in line with the uncertainty nature of risk, so it has more advantages.20 Fakhri, Yadolah used Monte Carlo method to evaluate the exposure of Pb and Cd in onion and soil from Iran.21 Qu C.22 based on the Monte Carlo method, took Qixia mining area as an example to evaluate the health risks of soil contaminated by heavy metals.

In this paper, 100 groups of CHS obtained from the local supermarkets and hotpot restaurants were taken as research objects. Nine kinds of metal element (Pb, As, Hg, Cd, Cr, Fe, Mn, Cu, Zn) were detected. Based on Monte Carlo simulation technology, the Crystal ball risk assessment software was used to evaluate chronic daily intake (CDI), carcinogenic risk, noncarcinogenic risk and sensitivity analysis. The exposure risk of nine metal elements in CHS for people of different ages in Chongging were evaluated. The risk assessment results of this study provides scientific basis for guiding the safe consumption of Chongging hotpot, and provides a theoretical basis for the development of safety-compliant CHS quality standards.

2. **Experimental**

2.1. Materials

One hundred different groups of samples including prepackaged and fresh spicy hotpot seasoning were purchased from the local market (12 groups) and hotpot restaurants (88 groups). Pb, As, Hg, Cd, Cr, Fe, Mn, Cu and Zn standard solutions were purchased from the National Standard Substances Center. Nitric acid (guarantee reagent), perchloric acid (analytical reagent), and 30% hydrogen peroxide (analytical reagent) were purchased from Chongqing Chuandong Chemical Industry (Group) Co., Ltd.

2.2. Methods

2.2.1. Determination of metal elements. The main paragraph text follows directly on here. Add 1 g CHS, 8 mL HNO3 and 0.5 mL HClO₄ into the high-pressure digestion tank, and after standing overnight, the mixture was heated for 2.5 h at 120-130 °C.²³ After the solution was clarified, the volume was fixed to 25 mL and was to be measured. Cu, Fe, Zn, Mn were determined according to the methods of flame atomic absorption spectrometry (FAAS) and Pb, Cr, Cd were determined according to the methods of graphite furnace atomic absorption spectrometry (GF-AAS). The above seven elements were determined by ICE3000 atomic absorption spectrometry (ThermoFisher, USA). During GF-AAS analysis, argon was used as inert gas, pyrolyticcoated graphite tubes with a platform and 5 µL matrix modifier were used. The matrix modifier was a mixture of 0.5% (w/v) ammonium dihydrogen phosphate (H2PO4NH4) and 1% (v/v) HNO3. Most of the matrix was removed before atomization with less interference. As and Hg were determined by AFS-970 two-channel atomic fluorescence spectrometer (Haiguang Instrument Comp., Beijing, China). During AFS analysis, 5% (v/ v) HCl was used as carrier liquid, and a mixture of 2% (w/v) potassium borohydride (NaBH₄) and 0.5% (w/v) sodium hydroxide (NaOH) was used as reducing agent.

In order to ensure the accuracy of data, each sample was repeated three times, and blank and standard substance (GBW-25) (from China National Standards Research Center) were compared. For every 20 samples measured, two standard samples were measured to verify the accuracy of the instrument. The standard curve shows a linear relationship within the concentration range, the regression coefficient $(R^2) > 0.999$, and the relative standard deviation <10%, indicating that the elemental analysis method is accurate and reliable. The average recovery of metal elements is 90-110%, which verifies the effectiveness of the method. All metal concentrations are measured on a natural weight basis (mg kg⁻¹). The detection limits (LOD) of Pb, As, Hg, Cd, Cr, Fe, Mn, Cu and Zn were 0.02, 0.001, 0.003, 0.001, 0.01, 0.75, 0.2, 0.2 and 1 mg kg^{-1} , respectively.

2.2.2. Consumption data and population weight data sources. Body weight, age, and consumption rate are important parameters for evaluating dietary exposure assessment.24 This study conducted a face-to-face survey of 2000 hotpot consumers in Chongqing, including 1000 males and 1000 females. According to age, the respondents were divided into children group (7-13 years old), adolescents group (14-17 years old), adults group (18-49 years old), and elderly group (50-78 years old). The survey data were processed by SPSS virson19 software. The consumption level of CHS of different groups was shown in Table 1.

2.2.3. Risk assessment

2.2.3.1. Exposure assessment. Exposure assessment is one of the most important components of the risk assessment process.25 In this study, nine metal elements in CHS were respectively used as the single source of chemical substances exposure. The chronic daily intake (CDI) was calculated according to the formula (1) using the Monet Carlo method.26,27 The daily CHS intake per capita (PIR) is based on the CHS consumption level survey data of different populations.

$$CDI = \frac{C_f \times PIR \times ABS \times EF \times ED}{bw \times AT}$$
 (1)

Table 1 CHS consumption level and body weight of different groups

	Consumption	level (g d ⁻¹)	Body weight	(kg)
Age	male	female	male	female
7–13 14–17 18–49 50–75	33.4-95.8 37.7-107.9 37-134.8 40.7-123.1	30.6-91.6 29.7-105.3 33.3-111.5 33.3-107.5	24.2-46.4 46.3-68.1 52.5-84.3 55.7-82.5	22.2-44.2 34.7-58.3 43-72.2 46.5-68.9

Table 2 Daily reference dose (RfD) of metal elements in CHS

Metal elements	Reference	RfD (mg per kg per bw per d)
Pb	JECFA, PWVI = 0.025 mg per kg per bw per d	0.0035
As	JECFA, BMDL $0.5 = 3 \mu g$ per kg per bw per d	0.003
Hg	JECFA, PWVI = 4 μ g per kg per bw	0.00057
Cd	JECFA, $PTMI = 0.025$ mg per kg per bw per month	0.00083
Cr	CNS, UL = 500 $\mu g d^{-1}$	0.0083
Fe	$CNS, UL = 40 \text{ mg d}^{-1}$	0.667
Mn	$CNS, UL = 11 \text{ mg d}^{-1}$	0.183
Cu	CNS, $UL = 8 \text{ mg d}^{-1}$	0.133
Zn	CNS, $UL = 40 \text{ mg d}^{-1}$	0.667

In the formula: CDI is the chronic daily intake, mg per kg per bw per d; C_f is the exposure concentration of 9 metal elements in 100 groups of CHS, mg kg⁻¹; PIR is the daily CHS intake per capita, kg d⁻¹; EF is the exposure frequency, day per year; ED is the exposure duration (determined by different age groups), year; BW is the body weight, kg; AT (AT = ED year * 365 days per year) is the pulling time, d; ABS is the intestinal and gastric absorption coefficient (default: 1).

2.2.3.2. Non-carcinogenic risk. Non-carcinogenic risk of element metals in CHS was evaluated by calculating hazard quotient (HQ).²⁸ In the formula (2): HQ is the food exposure safety index of metal elements in CHS, indicating the impact of food safety; RfD is the daily reference dose of metal elements in CHS. When the calculated HQ is equal to or less than 1, it is impossible to produce non-carcinogenic effects; If the HQ is greater than 1, it may have a non-carcinogenic effect on human health.^{25,26}

$$HQ = \frac{CDI}{RfD}$$
 (2)

Reference dose (RfD) refers to a dose that an individual can be continuously exposed to this level for a long time without being harmed. Joint FAO/WHO Expert Committee on Food Additives (JECFA) recommended tolerable daily intake (TDI) is 0.0035 mg per kg per bw per d for Pb, 0.00083 mg per kg per bw per d for Cd, 0.003 mg per kg per bw per d for As, 0.00057 kg per bw per d for Hg, 0.0083 mg per kg per bw per d for Cr.²⁹ According to the regulations of Chinese Nutrition Society (CNS), the tolerable upper intake levels (UL) of Fe, Zn, Cu and Mn in adults with 60 kg are 40 mg per d, 40 mg per d, 8 mg d⁻¹ and 11 mg d⁻¹ respectively.³⁰ Therefore, the RfD used in the HQ calculation of this study is shown in Table 2.

At the current stage of quantitative risk assessment of multiple chemicals, exposure to two or more chemicals may result in additive and/or interactions effect,^{31,32} so risk-increasing assumptions must be applied. In this study, the risk-increasing assumptions was determined using the hazard index (HI) and calculated according to formula (3).^{33–36}

$$HI = HQ_1 + HQ_2 \cdots + HQ_n \tag{3}$$

2.2.3.3. Carcinogenic risk. Carcinogenic risk refers to an individual's increased likelihood of developing cancer over a lifetime due to exposure to potentially carcinogenic substances. Formula (4) shows how to calculate the carcinogenic risk

$$Cancer risk = CDI \times SF \tag{4}$$

In the formula (4): CDI is the same as formula (1), mg per kg per bw per d; SF is the slope factor of carcinogenic elements, mg kg⁻¹ d⁻¹. Environmental protection agency (EPA) recommend that the SF of As, Cd, Pb are 1.5 mg kg⁻¹ d⁻¹, 6.3 mg kg⁻¹ d⁻¹, 0.009 mg kg⁻¹ d⁻¹, respectively.³⁷

2.2.3.4. Sensitivity analysis. Sensitivity analysis is an important part of risk assessment and the basis of risk management.³⁸ The influence of each variable parameter in the evaluation model on the simulation results is analyzed, so as to take control measures for the main influencing factors to reduce the risk.³⁹ Crystal Ball risk assessment software was used to analyze the sensitivity of consumers aged 7–78 years to the consumption of nine metal elements in CHS. The main factors considered in this experiment include the content of metal elements in CHS, daily intake of CHS, body weight, the exposure duration and pulling time.

2.3. Data analysis

Firstly, Monte Carlo technology Crystal ball software was used to determine the optimal fitting distribution of the

Table 3 Content and detection rate of nine metal elements in 100 groups of CHS^a

Metal elements	Content of metal element/mg kg ⁻¹	LOD/mg kg ⁻¹	Detection rate/%
Pb	0.01-1.130	0.02	92
As	0.003-0.045	0.001	100
Hg	0.0015-0.002	0.003	0
Cd	0.0005-0.160	0.001	45
Cr	0.005-3.080	0.01	99
Zn	0.500-35.664	1	92
Mn	0.1-11.603	0.2	98
Cu	0.100-5.819	0.2	99
Fe	0.375-74.358	0.75	92

^a Note: undetected results were expressed as 1/2 LOD.

Table 4 Probabilistic estimation of CDI (mg per kg per bw per d) to nine metal elements

	Ages		Mean		50%	75%	95%	Min	Max
b	7–13	Male	4.71×10^{-4}	3.94×10^{-4}	2.41×10^{-4}	5.32×10^{-4}	1.55×10^{-2}	2.97×10^{-6}	2.99 × 10
		Female	3.17×10^{-4}		1.56×10^{-4}	3.57×10^{-4}	6.87×10^{-3}	1.59×10^{-6}	1.30×10^{-1}
	14-17	Male	2.11×10^{-4}	2.28×10^{-4}	1.07×10^{-4}	2.37×10^{-4}	7.81×10^{-3}	1.84×10^{-6}	1.51×10^{-1}
		Female	2.44×10^{-4}		1.24×10^{-4}	2.85×10^{-4}	5.73×10^{-3}	1.54×10^{-6}	1.09×10^{-1}
	18-49	Male	2.29×10^{-4}	2.29×10^{-4}	1.06×10^{-4}	2.54×10^{-4}	5.51×10^{-3}	6.60×10^{-7}	1.05×10^{-1}
		Female	2.30×10^{-4}		1.06×10^{-4}	2.55×10^{-4}	6.10×10^{-3}	9.86×10^{-7}	1.17×10^{-1}
	50-78	Male	2.00×10^{-4}	2.02×10^{-4}	1.02×10^{-4}	2.27×10^{-4}	4.24×10^{-3}	9.24×10^{-7}	8.03×10^{-1}
		Female	2.05×10^{-4}		1.05×10^{-4}	2.34×10^{-4}	3.63×10^{-3}	1.36×10^{-6}	6.80×10^{-6}
		All		2.63×10^{-4}	1.31×10^{-4}	2.98×10^{-4}	6.92×10^{-3}	1.48×10^{-6}	1.32×10^{-1}
S	7-13	Male	2.56×10^{-5}	2.58×10^{-5}	1.92×10^{-5}	3.41×10^{-5}	1.47×10^{-4}	1.46×10^{-6}	2.40×10^{-1}
		Female	2.60×10^{-5}		1.94×10^{-5}	3.42×10^{-5}	1.62×10^{-4}	1.33×10^{-6}	2.70×10^{-1}
	14-17	Male	1.75×10^{-5}	1.87×10^{-5}	1.37×10^{-5}	2.33×10^{-5}	7.70×10^{-5}	1.56×10^{-6}	1.19 × 10
		Female	1.99×10^{-5}		1.50×10^{-5}	2.65×10^{-5}	9.60×10^{-5}	1.40×10^{-6}	1.51×10^{-1}
	18-49	Male	1.83×10^{-5}	1.85×10^{-5}	1.27×10^{-5}	2.39×10^{-5}	1.18×10^{-4}	7.23×10^{-7}	1.96 × 10
		Female	1.87×10^{-5}		1.32×10^{-5}	2.43×10^{-5}	1.19×10^{-4}	7.04×10^{-7}	1.99 × 10
	50-78	Male	1.66×10^{-5}	1.69×10^{-5}	1.26×10^{-5}	2.22×10^{-5}	7.47×10^{-5}	1.02×10^{-6}	1.15×10^{-1}
	00 70	Female	1.72×10^{-5}	2.03 // 10	1.31×10^{-5}	2.27×10^{-5}	7.73×10^{-5}	1.39×10^{-6}	1.19 × 10
		All	1.72 / 10	2.00×10^{-5}	1.49×10^{-5}	2.64×10^{-5}	1.09×10^{-4}	1.20×10^{-6}	1.76×10^{-1}
g	7-13	Male	2.92×10^{-6}	2.92×10^{-6}	2.46×10^{-6}	4.15×10^{-6}	1.14×10^{-5}	1.67×10^{-10}	1.69×10^{-1}
8	, 10	Female	2.92×10^{-6}	2.32 / 10	2.46×10^{-6}	4.11×10^{-6}	1.17×10^{-5}	4.86×10^{-11}	1.74×10^{-1}
	14-17	Male	1.93×10^{-6}	2.08×10^{-6}	1.72×10^{-6}	2.81×10^{-6}	5.68×10^{-6}	7.09×10^{-10}	7.54×10^{-1}
	14 17	Female	2.23×10^{-6}	2.00 × 10	1.92×10^{-6}	3.23×10^{-6}	6.66×10^{-6}	5.09×10^{-10}	8.77×10^{-1}
	18-49	Male	2.10×10^{-6}	2.10×10^{-6}	1.62×10^{-6}	2.94×10^{-6}	9.47×10^{-6}	3.05×10^{-10} 3.05×10^{-10}	1.44×1
	10 49	Female	2.10×10^{-6} 2.10×10^{-6}	2.10 × 10	1.65×10^{-6}	2.94×10^{-6} 2.93×10^{-6}	9.33×10^{-6}	5.64×10^{-10}	1.44×1 1.42×1
	50-78	Male	1.87×10^{-6}	1.90×10^{-6}	1.62×10^{-6}	2.69×10^{-6}	6.00×10^{-6}	2.68×10^{-12}	8.26×1
	30 70	Female	1.94×10^{-6}	1.90 × 10	1.68×10^{-6}	2.79×10^{-6}	6.00×10^{-6} 6.02×10^{-6}	4.53×10^{-10}	8.11×1
		All	1.94 \ 10	2.25×10^{-6}	1.89×10^{-6}	3.21×10^{-6}	8.29×10^{-6}	3.45×10^{-10}	1.19×1
d	7-13	Male	1.24×10^{-5}	1.24×10^{-5}	3.20×10^{-6}	1.06×10^{-5}	7.31×10^{-4}	5.85×10^{-9}	1.19×1 1.44×1
1	7-13	Female	1.24×10 1.25×10^{-5}	1.24 × 10	3.20×10^{-6} 3.15×10^{-6}	1.00×10^{-5} 1.02×10^{-5}	9.78×10^{-4}	8.38×10^{-9}	1.44×1 1.93×1
	14-17	Male	8.17×10^{-6}	8.74×10^{-6}	2.17×10^{-6}	6.86×10^{-6}	6.04×10^{-4}	3.93×10^{-9}	1.93×1 1.19×1
	14-17	Female	9.31×10^{-6}	6.74 × 10	2.17×10 2.42×10^{-6}	7.68×10^{-6}	6.67×10^{-4}	5.39×10^{-9}	1.19×1 1.31×1
	10 40	Male	8.45×10^{-6}	8.63×10^{-6}	2.42×10 2.09×10^{-6}	6.78×10^{-6}	4.62×10^{-4}	8.71×10^{-10}	9.06×1
	18-49	Female	8.80×10^{-6}	6.03 × 10	2.09×10 2.17×10^{-6}	7.24×10^{-6}	4.02×10 4.08×10^{-4}	1.60×10^{-9}	7.98×1
	50-78	Male	8.55×10^{-6}	8.42×10^{-6}	2.05×10^{-6}	6.60×10^{-6}	1.74×10^{-3}	8.14×10^{-9}	3.47×1
	30-76	Female	8.29×10^{-6}	0.42 × 10	2.03×10 2.10×10^{-6}	6.79×10^{-6}	4.13×10^{-4}	3.50×10^{-9}	8.08×1
		All	8.29 × 10	9.56×10^{-6}	2.10×10 2.42×10^{-6}	7.84×10^{-6}	7.51×10^{-4}	4.71×10^{-9}	1.48×1
	7 10		1.49×10^{-3}	9.56×10 1.51×10^{-3}	2.42×10 1.13×10^{-3}	1.94×10^{-3}	9.60×10^{-3}	-1.82×10^{-4}	1.48×1 1.62×1
r	7–13	Male	1.49×10 1.53×10^{-3}	1.51×10	1.13×10 1.14×10^{-3}	1.94×10 2.01×10^{-3}	9.60×10 1.31×10^{-2}	-1.82×10 -8.66×10^{-5}	1.62×1 2.30×1
	44.47	Female	1.01×10^{-3}	1.08×10^{-3}	7.97×10^{-4}	1.34×10^{-3}	5.57×10^{-3}	-8.66×10 -8.74×10^{-5}	2.30×1 9.11×1
	14–17	Male	1.01×10 1.16×10^{-3}	1.08×10	7.97×10 8.78×10^{-4}	1.34×10 1.51×10^{-3}	5.57×10 1.11×10^{-2}		9.11×1 1.98×1
	40.40	Female	1.16×10^{-3} 1.09×10^{-3}	4.00 40=3	8.78×10 7.75×10^{-4}	1.51×10^{-3} 1.41×10^{-3}	9.08×10^{-3}	-1.22×10^{-4}	1.98×1 1.59×1
	18-49	Male	1.09×10^{-3} 1.09×10^{-3}	1.09×10^{-3}		1.41×10 1.42×10^{-3}	9.08×10^{-2} 1.30×10^{-2}	$-1.52 \times 10^{-4} \\ -1.64 \times 10^{-4}$	1.59×1 2.38×1
	50 50	Female		0.00 10=4	7.72×10^{-4}				
	50-78	Male	9.58×10^{-4}	9.80×10^{-4}	7.49×10^{-4}	1.25×10^{-3}	4.88×10^{-3}	-6.68×10^{-5}	7.84×1
		Female	1.00×10^{-3}	4.47 40=3	7.77×10^{-4} 8.76×10^{-4}	1.30×10^{-3} 1.52×10^{-3}	5.94×10^{-3}	-1.04×10^{-4}	9.88 × 1
		All	1.04	1.17×10^{-3}	$8./6 \times 10^{-2}$	1.52×10^{-3}	9.03×10^{-3}	-1.21×10^{-4}	1.57 × 1
1	7–13	Male	1.81×10^{-2}	1.82×10^{-2}	1.43×10^{-2}	2.47×10^{-2}	1.05×10^{-1}	-1.82×10^{-2}	1.73 × 1
		Female	1.83×10^{-2}		1.44×10^{-2}	2.46×10^{-2}	1.24×10^{-1}	-1.17×10^{-2}	2.10×1
	14-17	Male	1.22×10^{-2}	1.30×10^{-2}	1.00×10^{-2}	1.66×10^{-2}	6.05×10^{-2}	-8.16×10^{-3}	9.66 × 1
		Female	1.38×10^{-2}		1.13×10^{-2}	1.89×10^{-2}	6.32×10^{-2}	-9.34×10^{-3}	9.83×1
	18-49	Male	1.29×10^{-2}	1.30×10^{-2}	9.41×10^{-3}	1.74×10^{-2}	1.01×10^{-1}	-1.11×10^{-2}	1.74×1
		Female	1.30×10^{-2}		9.65×10^{-3}	1.74×10^{-2}	1.10×10^{-1}	-1.02×10^{-2}	1.92×1
	50-78	Male	1.16×10^{-2}	1.18×10^{-2}	9.42×10^{-3}	1.58×10^{-2}	5.44×10^{-2}	-1.01×10^{-2}	8.51×1
		Female	1.19×10^{-2}	2	9.57×10^{-3}	1.62×10^{-2}	6.88×10^{-2}	-9.68×10^{-3}	1.14 × 1
		All		1.40×10^{-2}	1.10×10^{-2}	1.89×10^{-2}	8.58×10^{-2}	-1.11×10^{-2}	1.43×1
n	7–13	Male	3.34×10^{-3}	3.36×10^{-3}	2.35×10^{-3}	4.49×10^{-3}	2.44×10^{-2}	1.81×10^{-5}	4.15×1
		Female	3.38×10^{-3}	_	2.35×10^{-3}	4.47×10^{-3}	2.39×10^{-2}	1.48×10^{-5}	4.02×1
	14-17	Male	2.24×10^{-3}	2.42×10^{-3}	1.66×10^{-3}	3.06×10^{-3}	1.53×10^{-2}	1.31×10^{-5}	2.58×1
		Female	2.60×10^{-3}		1.88×10^{-3}	3.51×10^{-3}	1.54×10^{-2}	1.40×10^{-5}	2.52×1
	18-49	Male	2.20×10^{-3}	2.30×10^{-3}	1.60×10^{-3}	2.96×10^{-3}	1.52×10^{-2}	1.29×10^{-5}	2.56×1
		Female	2.40×10^{-3}		$\boldsymbol{1.58\times10^{-3}}$	3.17×10^{-3}	2.40×10^{-2}	1.00×10^{-5}	4.26×1
	50-78	Male	2.15×10^{-3}	2.21×10^{-3}	1.55×10^{-3}	2.90×10^{-3}	$\boldsymbol{1.68\times10^{-2}}$	1.47×10^{-5}	2.90×10^{-1}
		Female	2.27×10^{-3}		1.63×10^{-3}	3.09×10^{-3}	1.50×10^{-2}	7.62×10^{-6}	2.50×1
				2.57×10^{-3}	1.82×10^{-3}	3.46×10^{-3}	1.88×10^{-2}	1.32×10^{-5}	3.19×10^{-1}

Table 4 (Contd.)

	Ages		Mean		50%	75%	95%	Min	Max
Cu	7-13	Male	2.22×10^{-3}	2.26×10^{-3}	1.65×10^{-3}	2.80×10^{-3}	3.43×10^{-2}	1.58×10^{-5}	6.40×10^{-3}
		Female	2.30×10^{-3}		1.73×10^{-3}	2.94×10^{-3}	$\boldsymbol{1.99\times10^{-2}}$	5.30×10^{-5}	3.53×10^{-2}
	14-17	Male	1.45×10^{-3}	1.58×10^{-3}	1.12×10^{-3}	1.85×10^{-3}	8.72×10^{-3}	4.84×10^{-5}	1.46×10^{-2}
		Female	1.71×10^{-3}		1.31×10^{-3}	2.20×10^{-3}	1.70×10^{-2}	9.41×10^{-6}	3.05×10^{-2}
	18-49	Male	$\boldsymbol{1.55\times10^{-3}}$	1.54×10^{-3}	1.10×10^{-3}	1.99×10^{-3}	1.69×10^{-2}	4.20×10^{-5}	3.06×10^{-2}
		Female	1.54×10^{-3}		1.11×10^{-3}	1.99×10^{-3}	1.03×10^{-2}	3.60×10^{-5}	1.74×10^{-2}
	50-78	Male	1.40×10^{-3}	1.42×10^{-3}	1.07×10^{-3}	$\boldsymbol{1.82\times10^{-3}}$	9.95×10^{-3}	3.98×10^{-5}	1.71×10^{-2}
		Female	1.44×10^{-3}		1.09×10^{-3}	1.85×10^{-3}	1.02×10^{-2}	6.36×10^{-6}	1.76×10^{-2}
		All		1.70×10^{-3}	1.27×10^{-3}	2.18×10^{-3}	1.59×10^{-2}	3.14×10^{-5}	2.84×10^{-2}
₹e	7-13	Male	1.73×10^{-2}	1.75×10^{-2}	9.04×10^{-3}	2.02×10^{-2}	2.51×10^{-1}	1.50×10^{-4}	4.62×10^{-3}
		Female	1.77×10^{-2}		9.04×10^{-3}	2.02×10^{-2}	1.07×10^{0}	1.46×10^{-4}	2.11×10^{0}
	14-17	Male	1.18×10^{-2}	1.24×10^{-2}	6.34×10^{-3}	1.39×10^{-2}	3.34×10^{-1}	8.81×10^{-5}	6.41×10^{-1}
		Female	1.30×10^{-2}		7.19×10^{-3}	$\boldsymbol{1.55\times10^{-2}}$	2.82×10^{-1}	1.20×10^{-4}	5.34×10^{-1}
	18-49	Male	1.23×10^{-2}	1.23×10^{-2}	6.03×10^{-3}	1.41×10^{-2}	2.61×10^{-1}	$7.26 imes 10^{-5}$	4.94×10^{-1}
		Female	1.23×10^{-2}		6.02×10^{-3}	1.37×10^{-2}	2.90×10^{-1}	7.24×10^{-5}	5.53×10^{-1}
	50-78	Male	1.11×10^{-2}	1.13×10^{-2}	5.92×10^{-3}	1.30×10^{-2}	2.25×10^{-1}	9.01×10^{-5}	4.26×10^{-3}
		Female	1.15×10^{-2}		6.21×10^{-3}	1.36×10^{-2}	4.60×10^{-1}	1.32×10^{-4}	8.95×10^{-1}
		All		1.34×10^{-2}	6.97×10^{-3}	1.55×10^{-2}	3.97×10^{-1}	1.09×10^{-4}	7.64×10^{-1}

determination results of 9 metal elements in 100 groups of CHS; secondly, the simulation results of the mean and different exposure sites (50%, 75%, 95%) were obtained by 10 000 iterations; finally, the above simulation results were compared with RfD and SF.

3. Results and discussion

3.1. Metal element contents

Content and detection rate of 9 metal elements in 100 groups of CHS were shown in Table 3. The results showed that the detection rate of Hg was 0%, the detection rate of Cd was 45%, and the detection rate of other seven element metals was more than 90%. The contents of Pb, As, Hg, Cd, Cr, Zn, Mn, Cu and Fe were as follows: $0.01-1.130 \text{ mg kg}^{-1}$, $0.003-0.045 \text{ mg kg}^{-1}$, $0.0015-0.002 \text{ mg kg}^{-1}$, $0.0005-0.160 \text{ mg kg}^{-1}$, 0.005-3.080 mg kg^{-1} , 0.500-35.664 mg kg^{-1} , 0.1-11.603 mg kg^{-1} , 0.100- 5.819 mg kg^{-1} , $0.375-74.358 \text{ mg kg}^{-1}$. Among them, the maximum value of Pb in one group exceeded the maximum value (1 mg kg⁻¹) stipulated in the food pollutant limit of China's national food safety standard GB2762-2017.4 GB2762-2017 stipulated that the maximum limit of As was 0.5 mg kg⁻¹, and the determination value of As content in 100 groups of CHS were all lower than the maximum limit. However, the maximum limit values of Cd, Cr, Fe, Mn, Cu and Zn in CHS have not been found at home and abroad, so it is necessary to conduct risk assessment.

3.2. Risk assessment

The fitting distribution of the above metal elements content determination results was performed to determine the probability distribution. The results showed that Pb, Cd, Cu, Cr and Fe were lognormal distribution, As was beta distribution, Zn was max extreme distribution and Mn was gamma distribution.

Determination of Hg were all below the detection limit, so treated with uniform distribution.

According to different age groups, formula (1) is used to calculate the CDI of 9 metals in CHS. The results of 10 000 iterations using Monte Carlo simulation technology were shown in Table 4. The average CDI of Pb, As, Hg, Cd, Cr, Zn, Mn, Cu and Fe were as follows: 2.63×10^{-4} mg per kg per bw per d, 2.00×10^{-5} mg per kg per bw per d, 2.25×10^{-6} mg per kg. per bw per d, 9.56×10^{-6} mg per kg per bw per d, 1.17×10^{-3} mg per kg per bw per d, 1.40×10^{-2} mg per kg per bw per d, 2.57×10^{-3} mg per kg per bw per d, 1.34×10^{-2} mg per kg per bw per d. All the average CDI were lower than the RfD of each metal elements. The order of CDI was Zn > Fe > Mn > Cu > Cr > Pb > As > Cd > Hg. Zn had the highest average CDI value and Hg had the lowest average CDI value.

The CDI values of Pb, Hg and Cr ingested by different age groups through CHS were in the order of 7-13 > 18-49 > 14-17 > 50-78. The CDI values of As, Cd, Zn, Mn, Cu and Fe were in the order of 7-13 > 14-17 > 18-49 > 50-78. Compared with different genders in the same age group, the CDI of females was generally higher than males.

3.3. Non-carcinogenic risk

The non-carcinogenic risk in this study was assessed with HQ values at 50%, 75%, and 95% exposure sites. Non-carcinogenic risks of element metals from ingestion of CHS were shown in Table 5 and Fig. 1. Fig. 1 shown that mean HQ value of nine metal elements: Cr > Pb > Zn > Fe > Mn > Cu > Cd > As > Hg. Table 5 shown that 50% and 75% exposure sites HQ value were all less than 1. At the exposure site, 95% HQ values of As, Hg, Zn, Mn, Cu and Fe were all less than 1, Pb was all more than 1, Cd was more than 1 at 7–13 years old (female) and 50–78 years old (male), Cr was more than 1 at 7–13 years old (male and female),

Table 5 Probabilistic estimation of HQ and calculated HI for investigated elements

		7-13		14-17		18-49		50–78				
Metal elements	Exposure site	Male	Female	Male	Female	Male	Female	Male	Female	Total HQ	Contribution to HI (%) HI	
Pb	20%	$\textbf{6.90}\times 10^{-2}$					3.03×10^{-2}	2.91×10^{-2}		3.74×10^{-2}	3.06×10^{-1}	10^{-1}
	75%	1.26×10^{-1}	2	$\times 10^{-2}$	2	2	5.86×10^{-2}	5.35×10^{-2}	2	6.95×10^{-2}		
As	95% 50%	4.43×10 6.40×10^{-3}	6.46×10^{-3}	8	1.64×10 5.00×10^{-3}	1.57×10 4.24×10^{-3}	1.74×10 4.39×10^{-3}	4.20×10^{-3}	1.04×10 4.37×10^{-3}	1.98×10 4.95×10^{-3}	2%	
	75%	9.98×10^{-3}	9.98×10^{-3}	$\times 10^{-3}$			7.04×10^{-3}	6.52×10^{-3}		7.71×10^{-3}		
	95%	4.89×10^{-2}	5.39×10^{-2}	$ imes 10^{-2}$			3.98×10^{-2}	2.49×10^{-2}		3.63×10^{-2}		
Hg	20%	4.32×10^{-3}					2.90×10^{-3}	2.85×10^{-3}		3.32×10^{-3}	1%	
	75%	6.50×10^{-3}				•	4.49×10^{-3}	4.27×10^{-3}		5.02×10^{-3}		
	95%	2.00×10^{-2}			1.17×10^{-2}		1.64×10^{-2}	1.05×10^{-2}		1.45×10^{-2}		
Cd	20%	3.86×10^{-3}					2.61×10^{-3}	2.47×10^{-3}		2.91×10^{-3}	4%	
	75%	9.51×10^{-3}		6.12×10^{-3}			6.43×10^{-3}	5.96×10^{-3}		7.02×10^{-3}		
	95%	8.81×10^{-1}	1.18×10^0				4.92×10^{-1}	2.10×10^{0}		9.04×10^{-1}		
Cr	20%	1.36×10^{-1}	1.37×10^{-1}		1.06×10^{-1}	9.33×10^{-2}	9.30×10^{-2}	9.03×10^{-2}	9.36×10^{-2}	1.06×10^{-1}	46%	
	75%	2.05×10^{-1}	Ε.	1.43×10^{-1}	1.62×10^{-1}	_	1.49×10^{-1}	1.34×10^{-1}	1.38×10^{-1}	1.61×10^{-1}		
	95%	1.16×10^{0}		6.71×10^{-1}	$1.33 imes 10^{0}$		$1.57 imes 10^0$	5.88×10^{-1}	7.15×10^{-1}	$1.09 imes 10^0$		
Zn	20%	2.15×10^{-2}	2.16×10^{-2}	$1.51 imes 10^{-2}$	1.69×10^{-2}	1.41×10^{-2}	1.45×10^{-2}	1.41×10^{-2}	1.44×10^{-2}	1.65×10^{-2}	2%	
	75%	3.28×10^{-2}	3.26×10^{-2}		2.53×10^{-2}	2.25×10^{-2}	2.25×10^{-2}	2.10×10^{-2}	2.15×10^{-2}	2.50×10^{-2}		
	95%	1.58×10^{-1}					1.64×10^{-1}	8.16×10^{-2}		1.29×10^{-1}		
Mn	20%	1.28×10^{-2}	1.28×10^{-2}				$8.63 imes 10^{-3}$	8.47×10^{-3}		9.96×10^{-3}	5%	
	75%	2.12×10^{-2}			1.66×10^{-2}	1.40×10^{-2}	1.47×10^{-2}	1.37×10^{-2}		1.63×10^{-2}		
	95%	1.33×10^{-1}					1.31×10^{-1}	9.20×10^{-2}		1.02×10^{-1}		
Cu	20%	1.24×10^{-2}	1.30×10^{-2}				8.32×10^{-3}	8.07×10^{-3}		9.57×10^{-3}	4%	
	75%	1.84×10^{-2}			1.47×10^{-2}	1.31×10^{-2}	1.30×10^{-2}	1.21×10^{-2}		1.44×10^{-2}		
	95%	2.58×10^{-1}			1.27×10^{-1}	•	$7.72 imes 10^{-2}$	7.48×10^{-2}	$7.68 imes 10^{-2}$	1.20×10^{-1}		
Fe	20%	1.36×10^{-2}			1.08×10^{-2}		$9.03 imes 10^{-3}$	8.88×10^{-3}	9.31×10^{-3}	1.05×10^{-2}	7%	
	75%	2.50×10^{-2}	2.46×10^{-2}	$1.71 imes 10^{-2}$	1.91×10^{-2}	1.71×10^{-2}	1.68×10^{-2}	1.60×10^{-2}	1.67×10^{-2}	1.91×10^{-2}		
	95%	3.76×10^{-1}	$1.61 imes 10^0$	5.01×10^{-1}	$4.22 imes 10^{-1}$	3.91×10^{-1}	4.35×10^{-1}	3.38×10^{-1}	6.90×10^{-1}	5.95×10^{-1}		

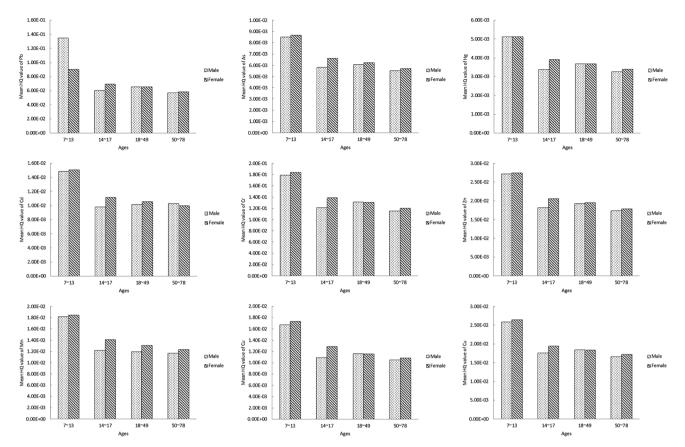


Fig. 1 Mean HQ value of nine metal elements

14-17 years old (female) and 18-49 years old (male and female). The results showed that humans will not have harmful effects on the 75% probability of ingesting these element metals through CHS, and 95% probability will only have harmful effects on some people. The average HI value of the nine element metals was 0.306 < 1, indicating that the overall risk of the nine element metals was safe. The contribution rate of Cr to HI value was the largest 46%, followed by Pb (25%), Zn and Fe (7%), and other element metals (5% or less).

Carcinogenic risk

Due to the lack of carcinogenic slope factors of Hg, Cr, Cu, Fe, Mn and Zn, this experiment only estimated the carcinogenic risk of three metal elements (As, Cd and Pb) in CHS. The mean carcinogenic risk values (standard deviation) As, Cd and Pb of children, adolescents, adults and the elderly were respectively as following: 3.87×10^{-5} (1.92 \times 10⁻⁴), 7.84×10^{-5} (2.60 \times 10^{-4}), 3.55×10^{-6} (7.43×10^{-6}), 2.80×10^{-5} (1.21×10^{-4}), 5.51 $\times 10^{-5} (1.75 \times 10^{-4}), 2.05 \times 10^{-6} (3.30 \times 10^{-6}), 2.78 \times 10^{-5}$ (1.55×10^{-4}) , 5.43×10^{-5} (1.69×10^{-4}) , 2.06×10^{-6} (3.64×10^{-6}) 10^{-6}), 2.53×10^{-5} (1.17×10^{-4}), 5.31×10^{-5} (2.76×10^{-4}), 1.82 \times 10⁻⁶ (3.10 \times 10⁻⁶). All cancer risks ranged from 1 \times 10-6 to 1 \times 10-4. In general, risks in the range of 1 \times 10⁻⁶ to 1 \times 10⁻⁴ were considered tolerable.40 Therefore, on the whole, the carcinogenic risk levels of As, Cd and Pb in CHS were acceptable.

3.5. Sensitivity analysis

Sensitivity analysis was performed on AT, ED, Cf, PIR and BW with Crystal ball software to determine the most important variables affecting the amount of health risk. Fig. 2 showed the results of a sensitivity analysis used to assess the noncarcinogenic risk of nine metal elements in CHS. The analysis results showed that Cf, PIR and BW were the main variables affecting the risk index except AT and ED (this is a pair of complementary parameters), among which the metal element content in CHS was the most sensitive (see blue bar in Fig. 1). The contribution rates of Pb, As, Hg, Cd, Cr, Mn, Cu, Zn and Fe to risk assessment were 55.5%, 31.3%, 39.6%, 74.1%, 33.2%, 47.2%, 31.6%, 39.7% and 54.4%, respectively. It can be seen that the content of each of the 9 metal elements in CHS is the most important factor that determines the risk index of ingesting metal elements. PIR was positively correlated with risk index, and its influence degree ranged from 4.1% to 12.0%, while body weight was negatively correlated with risk index. In general, it is particularly important to control the contamination of hotpot base materials and processing process to reduce the content of 9 element metals in CHS to ensure the safety of the exposure of dietary metal elements in hotpot.

Uncertainty analysis

Monte Carlo simulation was used to analyze the uncertainty of the estimated parameters. Through sensitivity analysis, it is

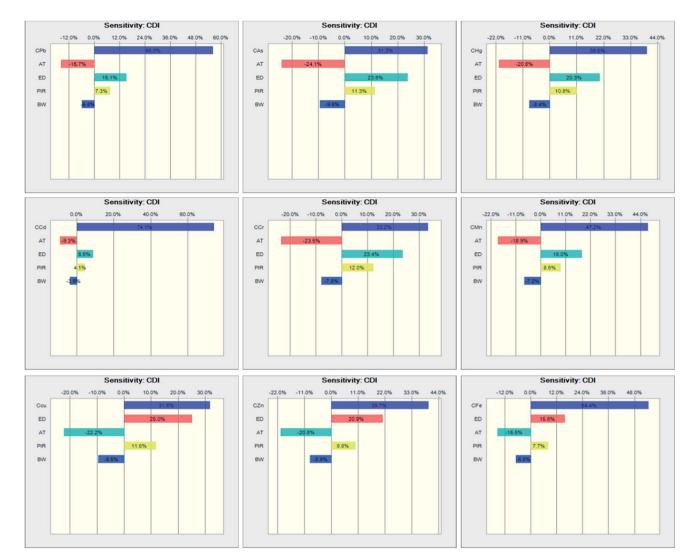


Fig. 2 Sensitivity analysis of metal element risk factors in CHS.

determined that the content of metal elements in the CHS, the daily dietary intake per capita and the per capita body weight of local residents are the main factors affecting CDI. The content of metal elements in the CHS depends on the brand, sampling area, selection and accuracy of measurement method. Due to the influence of sampling conditions and cost, this study only collected 100 groups of CHS in Chongqing for the measurement of metal element content. The limitation of sample size may lead to the uncertainty of metal element exposure risk assessment. All of the above results were based on the assumption that the diners will absorb all the metal elements contained in the CHS. However, when actually eating hotpot, the CHS was used after dissolving in water in a certain proportion, and the CHS was not directly eaten. Therefore, this hypothesis maximized the risk of experimental results. In addition, the selection of exposed population was only considered from the age difference and gender difference, and special groups such as pregnant women and sensitive groups with physical health defects were not considered, so the evaluation results were uncertain and limited to some extent. In future studies, it is

necessary to further expand the sampling scope, sampling scale, collection times, consumption data and other influencing factors, so as to make the conclusion of risk assessment of CHS more comprehensive and convincing.

4. Conclusions

Food safety risk assessment results are used in many ways, the most important of which is to serve as the scientific basis for the formulation and revision of food safety standards and the implementation of food safety supervision and management. In this study, Crystal ball software of Monte Carlo simulation technology was used to evaluate the risk of nine metal elements from a single source of CHS. Overall, the nine metal elements exposed to CHS pose no chronic toxicity risk to 90% of Chongqing residents. Pb, Cr and Cd bring less than 10% hazard risk to some people. It is worth noting that these probabilistic risks are the result of risk maximization. The variable that contributes the most to the sensitivity of risk index is the metal element content of CHS, which indicates that controlling the

contamination of CHS is especially important to ensure the safety of exposed food. The result of this risk assessment provides the theoretical basis for the formulation and revision of the CHS limit standard.

Conflicts of interest

There are no conflicts to declare.

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