Analysis and Risk Assessment of Heavy Metal Residues in Fish in Songhua River Basin

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Abstract. Thirty samples of crucian carp and carp are collected in upstream pine forest, midstream Dadingzi mountain and downstream Jiamusi section in the main stream of Songhua river. The ICP method is used to test heavy metals content of the fish. The exposure health risks of exposed way of edible fish in the Songhua River is assessed by exposure to the health risk assessment model. The results show that the noncarcinogenic target risk quotient (THQ) of each heavy metals is less than 1. The biggest heavy metal of the noncarcinogenic risk is As. From high to low in the order, the THQ is As>Cu>Mn>Pb>Cd. Composite exposure non carcinogenic hazard index (HIsF) is 0.18~0.23. As of fish exposed can cause the evident in the risk of cancer, TR is 2.89×10⁻⁵~6.78×10⁻⁵.

1. Introduction

The enrichment of heavy metals in edible fish is closely related to human health, and the accumulation of heavy metals in fish bodies can directly reflect the living water quality. In recent years, more and more studies have been conducted on the accumulation of heavy metals in cultured or wild fish and the potential exposure to human body and the health risks caused by it [1], especially the study on arsenic exposure. However, there are few studies on the combined exposure of heavy metals and health risk assessment [2]. In this paper, the distribution characteristics of heavy metals, heavy metal compound exposure levels and health risks of two kinds of main edible fish samples in state-controlled sections of Songlin river trunk stream were collected, so as to Preliminarily understand the edible safety of edible fish in the Songhua river trunk stream and provide reference and basis for relevant departments to formulate laws and regulations.

2. Materials and methods

2.1. Sample collection and processing

In April 2014, 30 samples of two species of crucian carp and carp were collected in Songhua River pine forest, Dadingzi Mountain and Jiamusi. Fishing methods vary depending on local conditions, and nets are often used to keep fish samples fresh. In the process of collection and transportation, low temperature preservation should be ensured, and samples should be prepared as soon as possible. Samples collected should be frozen and transported back to the laboratory for cryopreservation and treatment. Before processing the fish body, number each fish, weigh its length and weight, collect picture information, and record the basic information of the fish body in detail. The back muscles above the lateral line of the fish were collected for sample processing. The skin of the fish was
removed and the large spines were removed to make a sample, which was then stored under -18 in cold storage. Sample analysis by removing surface moisture, measuring and recording fish body length, body weight and other relevant information. The blank water was washed for more than 3 times. After drying, it was dissected with stainless steel dissecting knife soaked in 10% nitric acid solution for more than 24 hours, and the nonedible parts were removed, and the fish spines were removed, then put into the polyethylene bag and frozen for preservation.

2.2. Experimental reagents and instruments

Pure concentrated nitric acid was purchased from Shanghai sinopharm group.DEENA sample automatic digestion pretreatment system (Shanghai yizhen analytical instrument co., LTD.); Milli-Q purified water machine (Millipore, U.S.A); Inductively coupled plasma mass spectrometer (ICPS-7510, SHIMADZU, Japan).

2.3. Sample pretreatment

The dry weight of biological samples was determined by heating drying method. Calculate moisture content and dry/wet ratio (F). Through determination, the average moisture content of the fish sample was 73.01% and F was 0.257. Take a suitable amount of fish samples at 80 ℃ continuous baking in the oven for 10 h, grind into powder. Weigh about 2.0 g of fish powder into a 250 mL beaker, add 15mL of concentrated nitric acid and let stand overnight. 80 ℃ water bath 4 h, transfer and use the capacity in the experiment of water 50 ml volumetric flask and ICP-OES and engage detection.

2.4. Determination of the sample

Wet digestion and ICP-AES determination were carried out on fish muscle samples by experimental method. Six parallel samples were analyzed for each sample, and the results were shown in table 1.

| Fracture surface | Project name | Concentration range mg•kg⁻¹ | mean value mg•kg⁻¹ | GB2762-2005 Standard limit value | NY5073-2001 Standard limit value |
|-----------------|--------------|----------------------------|-------------------|---------------------------------|---------------------------------|
| Pinery          | As           | 0.0278~0.247              | 0.0495            | 0.1                             | 0.5                             |
|                 | Pb           | 0.0127~0.0719             | 0.0276            | 0.5                             | 0.5                             |
|                 | Cd           | 0.00013~0.00077           | 0.000284          | 0.1                             | 0.1                             |
|                 | Mn           | 0.38~0.46                 | 0.36              | —                               | —                               |
|                 | Cu           | 1.81~2.13                 | 1.97              | —                               | 50                              |
| Dadingzi mountain | As          | 0.0337~0.169              | 0.0809            | 0.1                             | 0.5                             |
|                 | Pb           | 0.0358~0.281              | 0.108             | 0.5                             | 0.5                             |
|                 | Cd           | 0.00031~0.00072           | 0.000817          | 0.1                             | 0.1                             |
|                 | Mn           | 0.27~0.44                 | 0.41              | —                               | —                               |
|                 | Cu           | 2.21~2.72                 | 2.51              | —                               | 50                              |
| Jiamusi         | As           | 0.0243~0.0637             | 0.0362            | 0.1                             | 0.5                             |
|                 | Pb           | 0.0334~0.231              | 0.0802            | 0.5                             | 0.5                             |
|                 | Cd           | 0.00012~0.00052           | 0.00023           | 0.1                             | 0.1                             |
|                 | Mn           | 0.27~0.44                 | 0.36              | —                               | —                               |
|                 | Cu           | 2.21~2.72                 | 2.37              | —                               | 50                              |
2.5. Quality control and quality assurance

The fish muscle solution to be measured after wet digestion was taken, and the same solution was measured 7 times in parallel, and the relative standard deviation of the results was calculated. A proper amount of standard substance was added to the solution under test, and the standard recovery was determined. The relative standard deviation was between 0.1% and 3%, and the standard recovery was between 92% and 112%.

3. Risk assessment of exposure to heavy metals in edible fish

3.1. Non-carcinogenic hazard assessment

The assessment of non-carcinogenic hazard caused by the enrichment of heavy metals in fish body by feeding route can be evaluated by risk coefficient (target hazard quotient, THQ) and non-carcinogenic risk coefficient (HI). The THQ calculation model established by USEPA[3]:

\[
THQ = \frac{C_b \times IR_F \times 10^{-3} \times EF_r \times ED_{tot}}{RfD \times BW \times AT_n}
\]

Where \(C_b\) is the heavy metal content in food, mg \(\cdot\) kg\(^{-1}\); \(IR_F\) is the unit quantity of intake through food, g \(\cdot\) d\(^{-1}\); \(EF_r\) is food intake frequency, 365 d \(\cdot\) d\(^{-1}\); \(ED_{tot}\) is the exposure interval, 70 a; \(RfD\) is the reference value, mg \(\cdot\) kg\(^{-1}\) \(\cdot\) d\(^{-1}\); \(BW\) is the average adult weight, kg; \(AT_n\) is the average time of exposure to non-carcinogenic risk, d. The reference dose recommended by USEPA[4] in 2000 is Pb=4µg \(\cdot\) kg\(^{-1}\) \(\cdot\) d\(^{-1}\); Cd=1µg \(\cdot\) kg\(^{-1}\) \(\cdot\) d\(^{-1}\); Zn=300µg \(\cdot\) kg\(^{-1}\) \(\cdot\) d\(^{-1}\); Cu=40µg \(\cdot\) kg\(^{-1}\) \(\cdot\) d\(^{-1}\).

The target risk quotient of the total amount of pollutants is the non-carcinogenic hazard index, and the calculation formula is as follows:

\[
\sum_{i=1}^{n} THQ = HIF
\]

\[
HI_{F} = \sum HI_{F}
\]

Where, \(HIF\) is the non-carcinogenic hazard index of fish exposed by a single pollutant in different ways; \(HI_{F}\) is the non-carcinogenic hazard index of fish eating exposed to multiple pollutants and multiple pathways, and \(THQ_i\) is the target risk quotient of the \(i\) pollutant. \(HI_{F}\) has the same evaluation criteria as THQ.

3.2. Carcinogen risk assessment

\(TR\) (target cancer risk) is used to represent the cancer risk, and its calculation formula is as follows:

\[
TR = \frac{C_b \times IR_F \times 10^{-3} \times CSF_o \times EF_r \times ED_{tot}}{BW \times AT_c}
\]

\[
TR_s = \sum TR_s
\]

Where, \(TR_s\) is the total risk of carcinogenesis; \(CSF_o\) is a carcinogenic slope factor of ingestion pathway, kg \(\cdot\) d \(\cdot\) mg\(^{-1}\); \(AT_c\) is the average exposure time of carcinogenic risk, d. Other meanings are the same as the previous. USEPA's belief that the safe carcinogenic risk range of pollutants is \(1 \times 10^{-6}\) ~ \(1 \times 10^{-4}\), and the risk control limit of \(TR_s\) is \(1 \times 10^{-6}\).

4. Results and discussion

4.1. Fish weight metal content

It can be seen from table 1 that the metal content of fish body from high to low is Cu > Mn > Pb > As > Cd. The enrichment degree of Cu and Mn is high, which is consistent with the composition characteristics of biological chemical substance. The content of Cd, As and Pb is relatively low, and these elements are non-essential elements for organisms, which are mainly concentrated in fish through intake, adsorption and other ways.
In terms of the content of Cu in organisms alone, the test results of fish in the Songhua river are similar to those of the yesilirmak river in Turkey [5], the cow lake in the United States [6] and the pearl river delta river network region [7]. Mn content of fish body is similar to that of the pearl river delta region, but significantly lower than that of the yesilirmak river in Turkey and swan lake in the United States [8]. The results of studies on Pb content in fish bodies of the yesilirmak river in Turkey, swan lake in the United States, river network area in the pearl river delta [9] and lake Tanganyika in Africa [10] are higher than the test results in this paper. The weight and metal content of fish in different regions are shown in table 2.

Table 2. Weight metal content of fish in different areas.

| Place                                      | As   | Pb   | Cd   | Mn   | Cu   | Data source          |
|--------------------------------------------|------|------|------|------|------|----------------------|
| Songhua River                              | 0.0208~0.3 | 0.0068~0.28 | 0.0001~0.02 | 0.38~0.46 | 1.81~2.1 | This research          |
| The yesilirmak river                       | —    | 0.10~0.56 | —    | —    | —    | Mendil                |
| The cow lake                               | —    | —    | —    | —    | —    | Aucoin                |
| The pearl river delta river network region | 0.17~1.46 | 0.05~1.94 | —    | 0.39~1.33 | 1.17~6.7 | Xie Wen-ping etc.      |
| Swan lake                                  | —    | 1.95~4.79 | —    | —    | —    | PARK                  |
| Tanganyika in Africa                       | —    | 4.9~5.30 | 0.2~0.65 | —    | —    | Chale                 |
| Pearl River Drainage Area                  | 0.53~3.44 | —    | 0.03~0.77 | —    | —    | Cheung                |

4.2. Health risk assessment of exposure to heavy metals in the fish-eating pathway

According to the IRIS database of USEPA, although As and Cd are carcinogenic substances, the main carcinogenic pathway is inhalation, and the carcinogenic effect caused by diet is not obvious. Due to the absence of Pb exposure toxicity data, this paper only calculated the carcinogenic risk of As TRₜₑ. The values of each parameter and its source in the health risk assessment model formula (1) and (4) of heavy metal exposure in the fish-eating pathway are shown in table 3, and the carcinogenic factors and reference dose are shown in table 4.

Table 3. The values of each parameter in the fish-eating health risk assessment model.

| Parameter | Numerical value | Source |
|-----------|-----------------|--------|
| IRₜₑ      | 36              | Statistics from the United Nations food and agriculture organization (FAO) |
| EFᵣ       | 350             | USEPA |
| EDₜₑₜᵣ    | 70 (1); 30 (2)  | USEPA |
| BWₐ        | 62.70           | document |
| ATₐ        | 10950           | USEPA |
| ATₗ        | 25550           | USEPA |

Note: (1) value of non-carcinogenic substances; (2) value of carcinogen.

Table 4. RfD and CSFo of fish feeding pathway exposed to heavy metals.

| Parameter | Cu      | Mn      | As      | Cd      | Pb      |
|-----------|---------|---------|---------|---------|---------|
| RfD mg⁻¹·kg⁻¹·d⁻¹ | 4×10⁻² | 1.4×10⁻¹ | 3×10⁻⁴ | 1×10⁻² | 3.57×10⁻³ |
| CSF₀ mg⁻¹·kg⁻¹·d⁻¹ | —      | —      | 1.5     | —       | —       |
| Source    | USEPA   | USEPA   | USEPA   | USEPA   | Document |
Table 5. THQ, HISF and TRAs exposed to heavy metals in the fish-feeding pathway.

| Fracture surface | Cu     | Mn     | As     | Cd     | Pb     | HISF (×10^{-5}) | TR_{As} (×10^{-5}) |
|------------------|--------|--------|--------|--------|--------|----------------|-------------------|
| Pinery           | 0.027  | 0.003  | 0.212  | 0.000  | 0.001  | 0.24           | 4.09              |
| Dadingzi mountain| 0.034  | 0.003  | 0.346  | 0.001  | 0.000  | 0.39           | 6.78              |
| Jiamusi          | 0.031  | 0.003  | 0.155  | 0.000  | 0.002  | 0.19           | 2.89              |
| Average value    | 0.030  | 0.003  | 0.237  | 0.000  | 0.001  | —              | —                 |

According to formula (1)–(5), the results of risk assessment are shown in Table 5. It can be seen from the THQ value in Table 5 that the THQ of heavy metal index is less than 1, indicating that the non-carcinogenic health risk caused by the single exposure of heavy metals in the fish-eating pathway is not obvious. The average value of THQ_{As} was the highest, and the average value of THQ_{Cd} was the lowest, indicating that the heavy metal with the highest risk of non-carcinogenic fish feeding pathway was As, while the contribution of Cd was the lowest [11].

From the HISF value of Table 4, we can see that the non-carcinogenic hazard index (HISF) of heavy metal compound exposure is less than 1, which indicates that the non-carcinogenic risk caused by heavy metal As, Cu, Mn, Pb and Cd combined exposure is lower. Long-term consumption of these fish causes less non-carcinogenic health hazards.

The carcinogenic risk TR of fish eating pathway As was all greater than 1×10^{-6}, with an average value of 2.89×10^{-5}–6.78×10^{-5}, indicating that the carcinogenic risk of As on human body through edible pathway was relatively obvious. This conclusion is consistent with the results of epidemiological studies. In general, the intake of arsenic through the fish-eating pathway is not only the largest factor of non-carcinogenic risk, but also has significant carcinogenic risk.

5. Conclusion
The non-carcinogenic health risks caused by single exposure of heavy metals in the fish feeding pathway in the Songhua river are not yet obvious. As is the metal element with the greatest non-carcinogenic risk in the fish-eating pathway, and also the element with the largest contribution to the non-carcinogenic hazard index of heavy metal compound exposure. The heavy metal THQ in the Songhua river was As>Cu>Mn>Pb>Cd from high to low. The non-carcinogenic hazard index HISF of the combined exposure of As, Cu, Mn, Pb and Cd heavy metals in the fish-feeding pathway ranged from 0.19 to 0.24. The average value of TR was 2.99×10^{-5}–6.68×10^{-5}.

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