Characteristics of heavy metals in surface water and assessment of water environment quality in the upper reaches of the Yellow River in recent 10 years

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Abstract. With the rapid development of economy, the load-bearing pressure of ecological environment is increasing, and human activities have brought tremendous challenges to surface water. In this paper, the surface water of 17 cities and counties in the upstream watershed of the reservoir in the source area of the Yellow River was taken as the research object. Based on the monitoring of the surface water quality section of the ecological transfer payment work in the national key ecological functional areas, surface water samples were collected quarterly from 2009 to 2018. Six heavy metal elements (cadmium, mercury, hexavalent chromium, lead, arsenic and copper) in surface water were analyzed in laboratory, and ArcGIS Kriging spatial interpolation method was used to study the spatial distribution characteristics of heavy metals in surface water in the upstream basin of the reservoir in the source area of the Yellow River. Meanwhile, the maximum membership degree method was used to evaluate the quality of water environment. The results showed that the spatial distribution of cadmium, mercury, hexavalent chromium, lead, arsenic and copper in the upstream basin of the reservoir in the source area of the Yellow River presented a dynamic change, and the high value of cadmium concentration appeared in the northeastern region of the evaluation area as a whole, showing a planar and strip distribution characteristics; the concentration values of mercury in the southwestern region of Maqu County and Luqu County were the highest, and in each county of the northeastern region were relatively lower. In the past 10 years, the average concentration of heavy metals in lead was 0.004 27 mg/L, and that in mercury was 0.000 4 mg/L. According to the maximum membership principle, the environmental quality of heavy metals in surface water in the upstream basin of the reservoir in the source area of the Yellow River in recent 10 years was superior.

1. Introduction

Water is the source of all life. It is precisely because of the water that this blue and beautiful planet is created, which enables human beings, animals and plants to survive. With the rapid development of economy, the load-bearing pressure of ecological environment is increasing, and human activities have brought tremendous challenges to surface water. Water pollution could be divided into two kinds: natural and man-made pollution[1]. Natural pollution refers to water pollution caused by natural causes. For example, earthquakes may cause some harmful elements of the earth's crust migrating to surface water or groundwater aquifers in large quantities, inducing surface water or groundwater...
pollution. Man-made pollution refers to the water pollution caused by waste materials in human production or living activities. In man-made pollution, industrial pollution is the main source of surface and groundwater pollution. Large amount of wastewater should be discharged in industrial production process, which is mixed with many raw materials, intermediate products or finished products, such as heavy metals, toxic chemicals, acids, bases, organic substances, oils, suspended substances, radioactive substances, etc., and all of these could cause pollution[2]. Additionally, there are also a lot of organic substances, pathogens and insect eggs in domestic sewage, and it also could cause water pollution when domestic sewage is discharged into water body or seeps into the ground. Heavy metals are common pollutants in water environment, and their anthropogenic origins are higher than natural origins. At present, many scholars have studied pollution of heavy metals in surface water. Wang Yanjie et al. studied pollution status of heavy metals such as mercury, zinc and lead in dongjiang, and the results showed that mass concentration of mercury in water body exceeded water quality standard of class III in the Environmental Quality Standards for Surface Water (GB3838-2002)[3]. Han Lingling et al. determined contents of copper, zinc and lead in water body of the Haizhou Bay, and the results showed that water body of the sea area has been slightly polluted by heavy metals[4]. As an important ecological barrier, upstream watershed of reservoir in the source area of the Yellow River guarantees the safety, survival and health of downstream groups[5-6]. In this paper, ecological transfer payment in the national key ecological functional areas was taken as an opportunity, and monitoring sites were set in main rivers, lakes and reservoirs of waterfront counties. Under the premise of obtaining large amount of scientific research data, the research work has been carried out.

2. Research data and methods

2.1. General situation of the research zone

The Yellow River is the second largest river of China, and its whole length is 5464 km. The Yellow River originated in Bayan Har Mountains of the Qinghai-Tibet Plateau, and mountain is dominant in upper and middle reaches of the Yellow River. Liujiaxia Reservoir is one of the largest reservoirs in source area of the Yellow River, and is in main stream of the Yellow River in Yongjing County of Gansu Province. It is 75 km from Lanzhou City, and the Taohe River, the Daxia River and other tributaries join its upper reaches. The region belongs to temperate semi-arid climate, and rainfall shows obvious seasonal distribution. It is arid season in spring and winter, with less rainfall, and it is level period during April-May. In summer, rainfall is more, and it is rainy season. During July-September, it is main flood season. Average rainfall for many years is 300-550 mm, while annual evaporation capacity is 1 500 mm. Main rivers in upper reaches of reservoirs in source area of the Yellow River contain main stream of the Yellow River, the Taohe River, and the Daxia River. The watershed contains six counties and cities of Gannan Tibetan Autonomous Prefecture (Maqu County, Luqu County, Zhuoni County, Lintan County, Xiahe County and Hezuo City), eight counties and cities of Linxia Hui Autonomous Prefecture (Linxia City, Linxia County, Jishishan County, Hezheng County, Dongxiang County, Guanghe County, Kangle County and Yongjing County), and three counties of Dingxi City (Minxian County, Lintao County and Weiyuan County), 17 counties and cities in total, and total area is 45 700 km².
Figure 1. These two figures have been placed side-by-side distribution of rivers in the upper reaches of reservoirs in the source area of the Yellow River

2.2. Sample collection and detection

According to distribution characteristics and status quo of watershed in upper reaches of reservoirs in source area of the Yellow River, surface water sample was collected quarterly from 2009 to 2018, and sampling sections were shown as Table 1. After water samples were collected, containers of packing water samples were immediately tightened, sealed and labeled (containing sampling site, sampling date and time, monitoring item and sampler). Detection indexes of water sample contained cadmium, mercury, hexavalent chromium, lead, arsenic and copper, and their analysis methods referred to the Environmental Quality Standards for Surface Water (GB 3838-2002).

Table 1. Sampling section name and analysis method

| Sampling section | Longitude /°E | Latitude /°N | Analysis content | Sampling time and frequency | Analysis method |
|------------------|---------------|--------------|------------------|----------------------------|-----------------|
| Maqu County (Zhuognima Yellow River Bridge) | 102.0814 | 33.9592 | Cadmium, mercury, hexavalent chromium, lead, arsenic and copper | Sampling and laboratory analysis of water quality monitoring was completed quarterly from 2009 to 2018, 40 times in total | Cadmium (atomic absorption spectrophotometry, GB7475-87), mercury (cold atomic absorption spectrophotometry, GB7486-87), hexavalent chromium (diphenylcarbazide spectrophotometric method, GB7467-84), lead (atomic absorption spectrophotometry, GB7486-87), arsenic (silver diethylidithiocarbamate spectrophotometry, GB7475-87), copper (sodium diethylidithiocarbamate spectrophotometry, GB7474-87) |
| Luqu County (Xicang Temple) | 102.547 | 34.388 | | | |
| Zhuoni County (Muer Town) | 103.5392 | 34.5636 | | | |
| Xiahe County (Digou Bridge) | 102.7997 | 35.3467 | | | |
| Hezuo City | 102.8714 | 35.1069 | | | |
| Lintan County (the Yemu River of Yeliguan) | 103.595 | 34.9519 | | | |
| Yongjing County (Fuhe Bridge) | 103.164 | 34.999 | | | |
| Yongjing County (center of Liujiaxia Reservoir) | 103.2872 | 35.4189 | | | |
| Jishishan County (Dahejia Bridge) | 103 | 35.827 | | | |
| Dongxiang County | 103.2589 | 35.6319 | | | |
| Linxia City (Shaangdongkou of the Daxia River) | 103.1808 | 35.56 | | | |
| Linxia County (Tumengguan) | 102.9417 | 35.4161 | | | |
| Hezheng County (the Danancha River) | 103.685 | 35.687 | | | |
Kangle County (the Suji River) 103.7067 35.3764
Guanghe County (the Guangtong River) 103.55 35.487
Lintao County (Yujing) 103.8192 35.2660
Lintao County (Taoyuan Bridge) 103.7860 35.5817
Weiyuan County (Luming Village of Wuzhu Town) 104.0939 35.0358
Weiyuan County (Sanhekou) 104.285 35.148
Minxian County (Xiazongzhai of Weixin Township) 103.8631 34.6875
Minxian County (Lengdi Village of Xizhai Town) 103.7914 34.4967

2.3. Quality assessment of heavy metals and water environment
Considering the selected research object, single factor was evaluated. Supposed that evaluation object was \( F \), and evaluation factor set was \( M = \{m_1, m_2, \ldots, m_q\} \), and evaluation grade was \( N = \{n_1, n_2, \ldots, n_p\} \), fuzzy assessment of each evaluation factor was conducted according to the limit of evaluation grade standard\([7-8]\), obtaining membership function:

\[
A = \begin{bmatrix}
a_{11}, a_{12}, \ldots, a_{1p} \\
a_{21}, a_{22}, \ldots, a_{2p} \\
a_{q1}, a_{q2}, \ldots, a_{qp}
\end{bmatrix}
\]

where \( a_{ij} \) showed membership of \( M_i \) to \( N_j \). \((M, N, A)\) constituted a fuzzy comprehensive evaluation model. To reflect overall situation of surface water in upper reaches of reservoirs in source area of the Yellow River, evaluation grade was divided into five levels \( (p = 5) \), and membership was calculated by using reduced half trapezoidal membership function (Table 2).

**Table 2. The formula of membership function**

| \( M_i \) section | I     | II    | III   | IV    | V     |
|-------------------|-------|-------|-------|-------|-------|
| \( m_i \leq n_i \) | 1     | 0     | 0     | 0     | 0     |
| \( n_1 < m_i \leq n_2 \) | \( \frac{n_2 - m_i}{n_2 - n_1} \) | \( \frac{m_i - n_1}{n_2 - n_1} \) | 0     | 0     | 0     |
| \( n_2 < m_i \leq n_3 \) | 0     | \( \frac{n_2 - m_i}{n_3 - n_2} \) | \( \frac{m_i - n_2}{n_3 - n_2} \) | 0     | 0     |
| \( n_3 < m_i \leq n_4 \) | 0     | 0     | \( \frac{n_4 - m_i}{n_4 - n_3} \) | \( \frac{m_i - n_3}{n_4 - n_3} \) | 0     |
| \( n_4 < m_i \leq n_5 \) | 0     | 0     | 0     | \( \frac{n_5 - m_i}{n_5 - n_4} \) | \( \frac{m_i - n_4}{n_5 - n_4} \) |
| \( m_i > n_5 \) | 0     | 0     | 0     | 0     | 1     |

Weight of each evaluation factor was determined based on comprehensively considering each factor, and it was marked as \( E = \{e_1, e_2, \ldots, e_n\} \). Via weighted average computation, a set of assessment feature could be obtained:
\[ F = E \cdot A = \sum_{i=1}^{n} (E_i \times a_i) = (f_1, f_2, ..., f_n) \]

where \( \sum_{i=1}^{n} e_i = 1 \).

According to the maximum membership principle, evaluation grade of evaluation object \( F \) was determined.

In order to facilitate the analysis and explanation of heavy metals in surface water of upper reaches of reservoirs in the source area of the Yellow River, classification was carried out according to the existing environmental quality standards promulgated by the state (Table 2).

**Table 3.** Standard for classification of heavy metals in surface water environment of upper reaches of reservoirs in the source area of the Yellow River

| Category       | Factor          | Superior | Good | Moderate | Worse | Bad       | Actual mean in the past 10 years |
|----------------|-----------------|----------|------|----------|-------|-----------|----------------------------------|
| Surface water  | Copper (mg/L) ≤ | 0.01     | 1    | 1        | 1     | 1         | 0.00201                          |
|                | Mercury (mg/L) ≤| 0.0005   | 0.0005 | 0.001   | 0.001 | 0.001     | 0.0004                           |
|                | Hexavalent chromium (mg/L) ≤ | 0.01     | 0.05 | 0.2      | 0.2   | 0.2       | 0.00691                          |
|                | Lead (mg/L) ≤   | 0.01     | 0.01 | 0.05     | 0.05  | 0.1       | 0.00427                          |
|                | Arsenic (mg/L) ≤| 0.05     | 0.05 | 0.05     | 0.1   | 0.1       | 0.00088                          |
|                | Cadmium (mg/L) ≤| 0.0001   | 0.0005 | 0.001   | 0.01  | 0.005     | 0.00047                          |

Relative pollution value method was used for calculation, and then normalization was conducted. Weight of single factor was determined:

\[ E_i = \frac{(M_i / N_i)}{\sum_{i=1}^{a} (M_i / N_i)} \]

\( M_i \) was monitoring value of parameter \( i \), and \( N_i \) was mean of standard value of environmental quality at each level of parameter \( i \), and \( E_i \) was weight of parameter \( i \).

According to laboratory analysis results and classification criteria, weights of cadmium, mercury, hexavalent chromium, lead, arsenic and copper were determined.

### 3. Results and analyses

#### 3.1. Spatial distribution characteristics of heavy metals in surface water

According to analysis results of different heavy metals in surface water of upper reaches of reservoirs in source area of the Yellow River in recent 10 years, spatial distribution of heavy metals in surface water was shown as Fig.2. It was clear that high value of cadmium concentration appeared in northeast region of the evaluation zone, containing Hanjishan, Yongjing, Dongxiang, Guanghe, Lintao, and Weiyuan, and cadmium concentration was lower in Xiahe, Lintan and Minxian. Spatial distribution of cadmium concentration overall showed planar and strip shapes. Spatial distribution of mercury showed contrary characteristics with that of cadmium, and mercury concentration was the highest in Maqu County and Luqu County of southwest region, and was relatively lower in each county of northeast region. Spatial distribution of hexavalent chromium was roughly similar to that of mercury, but the maximum was mainly in Maqu County, and it was relatively lower in Luqu County. Similarly, the concentration of hexavalent chromium in each county of northeast region was lower. Spatial
distribution of lead was similar to that of mercury, and high value appeared in Maqu County and Luqu County, and it showed circumferential characteristics in central region. Arsenic concentration was the highest in northwest region, and high value mainly appeared in Xiahe, Hezuo City and Jishishan, and there were obvious spatial distribution characteristics of strip shape. Copper concentration was the highest in Luqu County and was lower in other regions, and it showed isolated island distribution. Spatial distribution of cadmium, mercury, hexavalent chromium, lead, arsenic and copper showed dynamic change in upper reaches of reservoirs in source area of the Yellow River. Maqu County is main origin of the Yellow River, and different heavy metals showed high-value distribution characteristics in the county, and attention should be paid to by relevant management departments.

**Figure 2.** Spatial interpolation of heavy metals in surface water of upper reaches of reservoirs in the source area of the Yellow River in recent 10 years
3.2. Quality evaluation of surface water

Seen from surface water sample analysis in upper reaches of reservoirs in source area of the Yellow River, mean lead concentration was 0.00427 mg/L in recent 10 years, which was the highest, while mean mercury concentration was 0.0004 mg/L, which was the lowest. Surface water in upper reaches of reservoirs in source area of the Yellow River showed exceeding phenomenon of heavy metals. Classification was conducted according to classification standards, and cadmium, mercury, hexavalent chromium, lead, arsenic and copper all reached the first level. According to relative pollution value method, the weights of cadmium, mercury, hexavalent chromium, lead, arsenic and copper were respectively 0.176, 0.62, 0.065, 0.12, 0.016 and 0.003. Among them, weight of mercury was the highest, while weight of copper was the lowest. According to the maximum subordination principle, it could be judged that heavy metals in surface water of upper reaches of reservoirs in source area of the Yellow River in recent 10 years reached the first level. Monitoring results of different sections in surface water of upper reaches of reservoirs in source area of the Yellow River in recent 10 years were shown as Table 4.

Table 4. Monitoring results of different sections in surface water of upper reaches of reservoirs in the source area of the Yellow River

| Sampling section                                      | Means of heavy metals during 2009-2018 |
|-------------------------------------------------------|----------------------------------------|
|                                                       | Arsenic | Mercury | Hexavalent chromium | Cadmium | Lead   | Copper  |
| Maqu County (Zhuognima Yellow River Bridge)           | 0.00030 | 0.00007 | 0.01892              | 0.00010 | 0.0100 | 0.00325 |
| Maqu County (Zhuognima Yellow River Bridge 01)        | 0.00030 | 0.00007 | 0.01892              | 0.00010 | 0.0100 | 0.00325 |
| Maqu County (Zhuognima Yellow River Bridge 02)        | 0.00030 | 0.00007 | 0.01892              | 0.00010 | 0.0100 | 0.00325 |
| Luqu County (Xicang Temple)                           | 0.00102 | 0.00010 | 0.00717              | 0.00100 | 0.0100 | 0.01325 |
| Zhuoni County (Muer Town)                             | 0.00023 | 0.00003 | 0.00578              | 0.00007 | 0.00067 | 0.00067 |
| Xiahe County (Digou Bridge)                           | 0.00030 | 0.00004 | 0.00400              | 0.00100 | 0.00200 | 0.00100 |
| Hezuo City                                            | 0.00254 | 0.00002 | 0.01367              | 0.00050 | 0.00500 | 0.00050 |
| Lintan County (the Yemu River of Yeliguan)            | 0.00245 | 0.00002 | 0.00713              | 0.00050 | 0.00500 | 0.00050 |
| Yongjing County (Fuhe Bridge)                         | 0.00130 | 0.00004 | 0.00600              | 0.00010 | 0.00200 | 0.00300 |
| Yongjing County (Fuhe Bridge 01)                      | 0.00130 | 0.00004 | 0.00600              | 0.00010 | 0.00200 | 0.00300 |
| Yongjing County (center of Liujiaxia Reservoir)       | 0.00002 | 0.00002 | 0.00200              | 0.00005 | 0.00100 | 0.00050 |
| Jishishan County (Dahejia Bridge)                     | 0.00160 | 0.00004 | 0.00800              | 0.00010 | 0.00200 | 0.00100 |
| Dongxiang County                                      | 0.00110 | 0.00002 | 0.00200              | 0.00005 | 0.00100 | 0.00200 |
| Linxia County (Shuangdongkou of the Daxia River)       | 0.00178 | 0.00004 | 0.00725              | 0.00010 | 0.00175 | 0.00243 |
| Linxia County (Tumenguang)                            | 0.00250 | 0.00004 | 0.00600              | 0.00010 | 0.00200 | 0.00200 |
| Hezheng County (the Danancha River)                    | 0.00015 | 0.00002 | 0.00500              | 0.00050 | 0.00050 | 0.00050 |
Kangle County (the Suji River) & 0.00230 & 0.00002 & 0.01200 & 0.00005 & 0.00050 & 0.00050 \\
Guanghe County (the Guangtong River) & 0.00038 & 0.00002 & 0.00600 & 0.00005 & 0.00050 & 0.00375 \\
Lintao County (Yujing) & 0.00030 & 0.00004 & 0.00400 & 0.00010 & 0.00667 & 0.00167 \\
Lintao County (Taoyuan Bridge) & 0.00030 & 0.00004 & 0.00400 & 0.00010 & 0.00667 & 0.00167 \\
Weiyuan County (Luming Village of Wuzhu Town) & 0.00015 & 0.00004 & 0.00200 & 0.00050 & 0.00500 & 0.00050 \\
Weiyuan County (Sanhekou) & 0.00015 & 0.00004 & 0.00200 & 0.00050 & 0.00500 & 0.00050 \\
Minxian County (Xiazhongzhai of Weixin Township) & 0.00052 & 0.00002 & 0.00200 & 0.00050 & 0.00500 & 0.00050 \\
Minxian County (Xiazhongzhai 01 of Weixin Township) & 0.00052 & 0.00002 & 0.00200 & 0.00050 & 0.00500 & 0.00050 \\
Minxian County (Lengdi Village of Xizhai Town) & 0.00015 & 0.00002 & 0.00200 & 0.00050 & 0.00750 & 0.00050 \\
Mean & 0.00088 & 0.00004 & 0.00691 & 0.00047 & 0.00427 & 0.00201 \\

4. Conclusions
The spatial distribution of cadmium, mercury, hexavalent chromium, lead, arsenic and copper in the upstream of the reservoir in the source area of the Yellow River presented a dynamic change, and the high value of cadmium concentration appeared in the northeastern region of the evaluation area as a whole.

(1) Spatial distribution of cadmium, mercury, hexavalent chromium, lead, arsenic and copper showed dynamic change in upper reaches of reservoirs in the source area of the Yellow River. High value of cadmium concentration appeared in northeast region of evaluation zone, and it overall showed distribution characteristics of planar and strip shapes. Mercury concentration was the highest in Maqu County and Luqu County, and was relatively lower in each county of northeast region.

(2) In recent 10 years, mean lead concentration was 0.00427 mg/L, which was the highest, while mean mercury concentration was 0.0004 mg/L, which was the lowest. Surface water in upper reaches of reservoirs in source area of the Yellow River all showed the phenomenon of heavy metals exceeding standard. Classification was conducted according to classification standards, and cadmium, mercury, hexavalent chromium, lead, arsenic and copper all reached the first level. Weights of cadmium, mercury, hexavalent chromium, lead, arsenic and copper were respectively 0.176, 0.62, 0.065, 0.12, 0.016, and 0.003, and environmental quality of heavy metals in surface water of upper reaches of reservoirs in the source area of the Yellow River in recent 10 years was superior.

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