Residual arsenic in Yellow River fish and effects of suspended sediment

ZHANG SHUGUANG, LI YAQING & MU TAO
Yellow River Water Resources Protection Institute, 2 Chengbei Road, Zhengzhou, China

Abstract Sources of arsenic in the Yellow River were investigated with respect to the geochemistry of the sediment, the residual arsenic in fish and arsenic in water. Arsenic concentrations in the river water are highly correlated with the suspended-sediment concentration. In particular, the highest concentrations of arsenic are in the lower reaches of the river and are caused by the erosion of high-arsenic sediment from the loess plateau in the lower part of the middle reach. The residual arsenic concentrations in fish were related to the arsenic concentrations and suspended-sediment concentrations in water. In addition, a detailed investigation of the food consumed by the fish indicated that the more complex the food consumed by a fish, the higher the residual arsenic concentration in the fish.

INTRODUCTION

The Yellow River contains and transports large amounts of suspended sediment. The average annual sediment transport for the Yellow River is $1.6 \times 10^9$ t. The average annual suspended-sediment concentration is about $38 \text{ kg m}^{-3}$, which is the highest, on average, of any river in the world. The large amount of sediment not only causes unique problems for developing and using water resources, but also causes many adverse effects on aquatic resources. In addition, high concentrations of pollutants occur through absorption and chelation by clay mineral, carbonate and metal hydrate oxide in the sediment.

Previous studies indicate that the arsenic in the Yellow River originates primarily from eroded sediment from the middle loess plateau, a vast area marked by serious water and erosion problems. The sediment-associated arsenic contributes about $160 \times 10^6$ t. In contrast, the mean annual concentration caused by anthropogenic pollution is only at the ppb level. The high arsenic concentrations and loads in the Yellow River occur naturally. The residual arsenic concentration in fish is higher in the lower reaches of the Yellow River than in the upper and middle reaches. The residual arsenic concentrations in fish are highly correlated with the arsenic concentrations in water. And the highest concentrations in fish are related to the complexity of the food consumed with the lowest arsenic concentrations in fish which feed on the simplest organisms. And it has the phenomena of synchronous level very similarly between the arsenic in fish and the sediment contents in the Yellow River. Results of an investigation of the source of dissolved arsenic in the Yellow River and residual arsenic in Yellow River fish are reported in this paper.
METHODS AND MATERIALS

Study area

In order to understand the processes controlling the residual arsenic concentrations in fish of the Yellow River, arsenic concentrations were determined for river water sampled from headwaters to the ocean. Several other factors including hydrography, sediment sources, geomorphology, and water management practices were evaluated to determine an optimum sampling strategy and to aid in the data interpretation. Nineteen sampling stations were chosen for study from Maqu in the upper reach to Lijin at the mouth the Yellow River for analysing the residual arsenic in fish (Fig. 1). In addition, the arsenic content of solids was determined for the soils in eight Provinces (counties) of the Yellow River basin, and sediment, peat and bedrock were collected at some of the stations as part of another study at the Institute.

Procedures

The fish that were sampled from the Yellow River were primarily those harvested for human consumption including carp, crucian carp, and cat fish. The fish muscles were digested with perchloric acid and nitric acid, and arsenic content was determined by silver salt colorimetry.

The river water in the Maqu reach, located in a non-polluted region of the Gannan Autonomy at 3500 m a.s.l., was sampled to provide background water quality information. Background arsenic concentrations in fish were determined from fish sampled in non-polluted pools near Yincuan and Zhangzhou. The water and sediment were analysed using standard methods.

RESULTS AND DISCUSSION

The residual arsenic in Yellow River fish

The arsenic concentration in the Yellow River was monitored at many sites from Qinghai Province at Xunhua to the ocean, more than 4000 km² downstream. Arsenic concentrations of the river at most stations exceeded the surface water quality standards. In particular, arsenic concentrations increased markedly in the middle reach of the river around Jin Shan and Meng which are adjacent to the loess plateau. The high arsenic concentrations in the river and the high economic value of the fish, including fish as a food source, require a more thorough evaluation of the effect of the arsenic on the fish, such as the dose/response relations and rates of enrichment, and public health impacts related to fish consumption and economic impact from the loss of fish as a food source. The arsenic concentrations in fish are shown in Fig. 2.

Results indicate that arsenic generally accumulates in the fish. Depending on the station, from 81 to 100% of the fish sampled contained detectable arsenic concentrations. Consistently high arsenic concentrations occurred from Longmen reach to lower Yellow River. The mean arsenic concentration in fish for all fish sampled was 0.265 mg l⁻¹. The highest residual arsenic concentration observed was 0.585
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Fig. 1 Sampling sites in the Yellow River.
mg kg\(^{-1}\) which exceeds the health standard for consumption (0.5 mg kg\(^{-1}\)). Somewhat surprising was the high arsenic concentrations in fish from the Yinchuan reach (Fig. 2), but further examination revealed higher arsenic contents in soils in the area and high irrigation return flows.

The main source of arsenic in Yellow River fish

Toxicants can be transferred and enriched in fish several ways including surface transfer, ingestion, or inhalation. Each mechanism is affected by the concentration of arsenic in the water of the Yellow River. Therefore, arsenic concentrations in the river were examined with respect to sources and compared with the arsenic concentrations in fish. The primary sources of arsenic in the Yellow River water that were examined include natural release associated with soil erosion and anthropogenic contributions associated with pesticide applications and industrial waste releases.

For many years, arsenic concentrations in the Yellow River have exceeded the water quality standard. In fact, the arsenic concentrations in what have previously considered to be background waters from the Yellow River also have exceeded the water quality standard. It, therefore, seemed plausible that the high arsenic concentrations result from a natural condition. An evaluation of arsenic content of the suspended sediment in the Yellow River, particularly that derived from the loess plateau, which is vast area with major problems of water management and soil erosion, was an important step in understanding the high arsenic concentrations in the river. According to previous studies (Yellow River Resources Protection Office, 1977), the mean arsenic concentration of the suspended sediment was 10.4 ppm in the middle reach of the Yellow River adjacent to the loess plateau, which is 1 time greater than the mean concentration in the upper lithosphere. Given this concentration and an annual sediment load of \(1.6 \times 10^9\) t, the total annual arsenic transported on sediment
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in the Yellow River is about $16 \times 10^3$ t. For comparison, the average annual arsenic concentration at Huayuankou on the lower Yellow River was 0.340 mg l$^{-1}$ and runoff was $47 \times 10^9$ m$^3$.

As for the anthropogenic sources, environment statistics from 1980 to 1983 indicate that industrial wastes from Yinghai, Gansu, Ningxia, Neimeng, Shanxi, and Henan Provinces contributed a total of 131.9 t of arsenic to the basin of the Yellow River. Industrial waste in Gansu Province alone produced 73 t of arsenic, which was 55% of the total. Although incomplete, 187 450 t of pesticides were sold in 293 counties throughout the basin during the five years from 1976 through 1980, which averages 37 490 t annually. Although the exact arsenic concentration was not determined for each type of pesticide used during this period, the arsenic concentration of the pesticide used in 15 counties of Sanxi Province in 1974 was 0.7%. Given the average annual sales for the region and applying the average arsenic concentration of the pesticides from Sanxi Province to those of the region, the pesticides could have contributed about 151.9 t of arsenic to the basin of the Yellow River. If all of the pesticide and industrial arsenic were to have reached the Yellow River each year, the average annual contribution from these sources would have been 283.8 t. Given the volume of discharge of the Yellow River, arsenic concentrations in the Yellow River produced from manmade sources would only attain a parts per billion level (Gao Chuande, 1986).

The concentrations of arsenic and suspended-sediment at stations along the main channel of the Yellow River are shown in Fig. 3. Note that arsenic is present at relatively high concentrations at every sampling station and that the concentrations below Qinghai Province are considerably higher than in higher reaches. In fact, the arsenic concentrations exceed water quality standards at several locations in the lower part of the river. The section of the river from Xunhua to Xiachengwan is marked by the lowest arsenic concentrations, i.e. those that have not exceeded the water quality standard for surface water. The second section from Baotou to the ocean is marked by high arsenic concentrations which typically were much greater than the water quality standard. The highest concentration (0.161 mg l$^{-1}$) occurs in the reach at Huayuankou. Arsenic concentrations in the Yellow River correlate with geography and, in particular, the associated suspended-sediment concentrations. The relatively high arsenic concentration (0.013 mg l$^{-1}$) in the headwaters along the reach at Xunhua is probably caused by high arsenic sediment eroding into the river from an arsenic mine. The lowest arsenic concentration (0.002 mg l$^{-1}$) for any location along the river was in the Liujiaxia Reservoir and is attributed to the loss of sediment by settling in the reservoir. Arsenic concentrations remain low (0.006 mg l$^{-1}$) from the outlet of the reservoir to downstream of Lanzhou due to little addition of water and sediment. At the Yinchuan Plain of the Ningxia Autonomous Region, arsenic concentrations increase markedly because the arsenic content in the soil eroded from the Yinchuan Plain is higher and the erosion is exacerbated by extensive irrigation. Below the Yinchuan Plain arsenic concentrations decrease partly because the sediment derived from the land in along this reach contains low concentrations of arsenic. For example, the Rendouosi Plateau in the south consists of sandy drift and bedrock with relatively low arsenic content (the arsenic concentration in some drift sand is only 1-2 mg kg$^{-1}$). Also, considerable amounts of water are withdrawn from the river for irrigation along this reach, which removes the arsenic. In the middle reach after Twoketuo, arsenic
concentrations increase markedly. The arsenic increase results from erosion of high-arsenic sediment from the loess plateau. The loess plateau contributes 90% of the total sediment in the water. The high contribution of sediment with high arsenic content causes river water concentrations to greatly exceed the water quality standard. Downstream the arsenic concentrations decrease somewhat (0.045 mg l\(^{-1}\)) from dilution by precipitation, although they remained above the water quality standard. Arsenic concentrations increase markedly again further downstream at Hauyuankou. The increase in the lower reach at this station is attributed to transport of high arsenic sediment from the loess plateau and resuspension of high arsenic sediment which was previously deposited in the reservoir.

In summary, the dissolved arsenic concentrations are highly correlated with suspended-sediment concentrations. Also, the arsenic concentrations on the suspended sediment correlate well with those of local sources, primarily soil. The residual arsenic concentrations in fish roughly correlate with the arsenic concentrations in water.

**The relation between sediment and the arsenic contents in water**

As previously discussed the primary source of the arsenic in the Yellow River is