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Variations of Arsenic Species Concentrations in Riverbed Sediments Induced by Geothermal Wastewater Drainage: A Case Study at the Yangbajing Geothermal Field, Tibet, China

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ABSTRACT

The high-temperature geothermal fluids from the Yangbajing field, a world famous geothermal field in Tibet, have been used for electricity generation. The geothermal wastewaters generated by the Yangbajing power plants with arsenic (As) concentrations up to 3.18 mg/L, were drained immediately into the Zangbo River, the major surface water in the study area, which markedly increased the arsenic concentration of river waters at the nearest downstream of the wastewater draining exit of the first power plant. However, along the flow direction of the Zangbo River, the arsenic concentrations in river waters were declining sharply. Further inspection shows that the concentrations of ionically bound As, strongly adsorbed As, and total As in riverbed sediments of the Zangbo River were also affected by the drainage of geothermal wastewaters, indicating that they may serve as one of the sinks of arsenic with geothermal source. In other words, after arsenic from geothermal wastewaters entered the Zangbo River, the adsorption of arsenic on riverbed sediments could lower the arsenic concentrations of river waters, which was helpful for reducing the health threat of arsenic on local residents with the Zangbo River as drinking water source.

1. INTRODUCTION

As a worldwide environmental issue, arsenic (As) enrichment is of great concern in the international community of environmental studies, due to the chronic effects of arsenic poisoning on people who are exposed to arsenic with high concentration. It has been proved that skin diseases and cardiovascular, neurological, hematological, renal and respiratory diseases can be induced by arsenic poisoning. More seriously, some cancers, such as lung, bladder, liver, kidney and prostate cancers may also result from exposure to arsenic (Morton and Dunette, 1994). In view of the severe health hazards of environmental arsenic, the World Health Organization (WHO) recommended in the 1980s that the upper limit of As concentration in drinking water should be 0.05 mg/L (WHO, 1984), and this limit was revised to 0.01 mg/L in the middle 1990s due to safety consideration (WHO, 1996). Furthermore, in recent years, arsenic has been ranked among the top 20 most hazardous, high priority substances by the Agency for Toxic Substances and Disease Registry (ATSDR, 2005). To better understand the mechanism of arsenic enrichment in environment, many scholars have carried out detailed research work on migration and transformation of environmental arsenic (Smedley and Kinniburgh, 2002; Arnórsson, 2003; Stüben et al., 2003; Szramek et al., 2004; Haque and Johannesson, 2006; Wang and Mulligan, 2006; Kouras et al., 2007; Smedley et al., 2007; Guo et al., 2008; Peters and Burkert, 2008).

It is commonly considered that environmental arsenic originates mainly from human activities (such as metal smelting, coal burning, exploitation of arsenic bearing minerals, and utilization of arsenic bearing pesticides) or natural processes (volcanic activities, weathering of surface rocks, and release of arsenic during water-rock interaction in groundwater system). Moreover, arsenic from geothermal water systems is now attracting more and more attention. It has been reported that the arsenic concentration in geothermal water from Ischia Island of southern Italy can be up to 1.56 mg/L (Lima et al., 2003), and that from Tokaanu of North Island of New Zealand 5.20 mg/L (Hirner et al., 1998). More surprisingly, the geothermal brine from Akita prefecture, northwestern Honshu Island of Japan has arsenic concentration as high as 13 mg/L (Pascua et al., 2007), and that from the El Tatio geothermal field of Chile 27.0 mg/L (Romero et al., 2003). So generally speaking, the arsenic concentrations in geothermal fluids are usually high, especially for those high-temperature geothermal systems with magma as their heat sources. Thus, geothermal spring discharge or geothermal wastewater drainage may not only be one of the major sources for arsenic in environment, but only have an extremely serious menace to human health. There are many high-temperature geothermal systems in western China where the geothermal waters with high arsenic concentrations occur, such as the Yangbajing geothermal field (Tibet), the Yangyi geothermal field (Tibet), and the Rehai geothermal field (Yunnan). However, there have been so far no systematic studies in China that focus on the migration, transformation and enrichment of environmental arsenic with geothermal sources. Therefore, in this study, the Yangbajing geothermal field, one of the most famous fields in Tibet, was chosen as the study area to discuss the environmental impact of geothermal waters with high arsenic concentration up to 5.70 mg/L (Guo et al., 2007).

The Yangbajing geothermal field is located to the northwest of Lhasa city, Tibet, western China and divided into the north area and the south area by China–Nepal Highway (Figure 1). The Zangbo River as the main surface water in the field winds towards the east on the southeast margin of the geothermal field and flows into the Brahmaputra River at the end. Before the first and second Yangbajing geothermal power plants were built (in 1981 and 1986 respectively), there were strong manifestation of hydrothermal activity in the field, including numerous boiling springs, hot springs, warm springs, and a hot lake. At that time, hot springs were the major discharge way of the geothermal waters. However, with the beginning of geothermal electricity generation, intensive artificial exploitation by the power plants, instead of natural springs, became the dominant discharge way of the thermal waters. At present, the geothermal waste waters generated by the power plants have been directly discharged into the Zangbo River, posing a threat to the water quality safety downstream.

2. SAMPLING AND ANALYSIS

Fifteen riverbed sediment samples were collected in the study area. Among these samples, ten were sampled in August of 2007 along the Zangbo River and its two tributaries where the wastewaters of the second power plant were drained, and five in June of 2006 along the Zangbo River. The sampling locations can be seen in Figure 1.

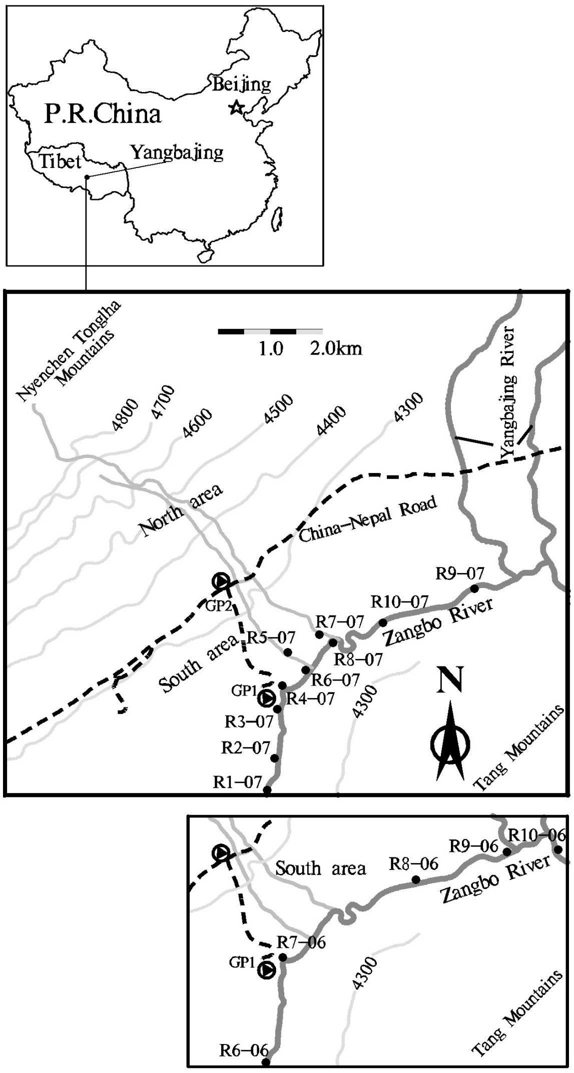

Figure 1: Simplified map of the study area and sampling locations. GP1 and GP2 represent the first and the second Yangbajing geothermal power plants, respectively. The figures on the map indicate the elevations of the area.

Moreover, in the sampling locations of R2-07, R3-07, R10-07, and R9-07, water samples were also collected for As analysis (in August 2007). So were two water samples from the wastewater draining exits of the first and second power plants (see GP1 and GP2 in Figure 1). Before Zangbo River water samples were collected, several large rainfalls occurred at the study areas, so the samples can only represent the situation in rain season. The measurements of As concentration in all water samples were completed using Atomic Fluorescence Spectrometer (AFS) (Type AF-610).

The As-bearing solid phases in all sediment samples, including ionically bound As and strongly adsorbed As, were extracted using sequential chemical extraction procedure recommended by Keon et al. (2001). The detailed extraction procedures were given as follows.

For the extraction of ionically bound As from sediment, a 0.25 g sediment subsample was added to a 50-ml polypropylene centrifuge tube along with 25 ml $MgCl_2$ extractant whose concentration and pH value are up to 1 mol/L and 8 respectively. The sediment vs extractant ratio of 1:100 (0.25 g to 25 ml) was applied in the experiment to prevent the extractant being exhausted. In the sealed centrifuge tube, the mixed solution was tumble-shaken for 2 hours and centrifuged for 20 min at 6000 r/min. The supernatant was removed from the centrifuge tube using pipette tips and then filtered through 200-nm polycarbonate filters. Afterwards, the same procedure was repeated twice and the remaining residue was washed using deionized water. Finally, the supernatants from all steps were put together and acidified to 1% with concentrated HCl for AFS analysis.

For the extraction of strongly adsorbed As, 25 ml NaH_2PO_4 solution with concentration and pH value up to 1 mol/L and 5 was employed as extractant. The mixed solution was tumble-shaken for 24 hours and centrifuged for 20 min at 6000 r/min. The supernatant was removed from the centrifuge tube and filtered through 200-nm polycarbonate filters. Then the same procedure was repeated once and the remaining residue was washed using deionized water. Similarly, the supernatants from all steps were put together and acidified to 1% with concentrated HCl for AFS analysis.

Besides, the total As in all sediment samples were also extracted. During the extraction experiment, a 0.1 g sediment subsample was put into a 25-ml colorimetric tube along with 5 ml nitrohydrochloric acid as extractant. Then the colorimetric tube was heated in water bath for 2 hours, and within this period the tube was shaken every 5 minutes. Finally, the extracting solution was mixed with 5 ml reductant (5% thiourea and 5% ascorbic acid) for AFS analysis.

After the extraction procedure, the arsenic concentrations of different extracting solutions were all determined using Atomic Fluorescence Spectrometer (Type AF-610). The results of measurement were then converted into the concentrations of ionically bound As, strongly adsorbed As, and total As in sediment samples. It is worth noting that replicate analyses of ionically bound As, strongly adsorbed As, and total As were made for selected sediment samples (R1-07 and R6-06), the results indicating that the analytical accuracy can satisfy our demand (the differences between two analyses are all less than 5%).

3. RESULTS AND DISCUSSION

According to our measurements, the geothermal wastewaters drained by the first and second power plants have arsenic concentrations up to 2.68 and 3.18 mg/L, respectively. Under the effect of wastewater drainage, the arsenic concentration of the Zangbo River water at the nearest downstream of the wastewater draining exit of the first power plant (the sampling location of R3-07) are up to 0.20 mg/L, far more than that (0.01 mg/L) at the upstream of the exit (the sampling location of R2-07). However, the arsenic concentrations of the river waters decline sharply in the downstream and are 0.07 and 0.06 mg/L at the sampling locations of R9-07 and R10-07, respectively, indicating that there may exist a migration of arsenic from river waters to riverbed sediments. Furthermore, according to our field estimates, there are several clean tributaries whose dilution was contributing to the loss of arsenic in Zangbo River waters. However, the total flow volume of these tributaries are far less than that of Zangbo River, so their dilution is absolutely not the only factor causing the arsenic concentration decline in Zangbo river (from 0.20 mg/L to 0.07 mg/L). In other words, the adsorption of riverbed sediments is also a non-negligible factor. To prove this issue, the variations of ionically bound As, strongly adsorbed As, and total As in the riverbed sediments were discussed below.

Based on the statistical results, the concentrations of ionically bound As in all riverbed sediment samples range from 0.03 to 12.4 ppm, with the average value of 2.43 ppm, and those of strongly adsorbed As are between 0.68 and 111.9 ppm, the average value being 29.7 ppm. Correspondingly, the maximum, minimum and average concentrations of total As in all sediments are 187.5, 2.65, and 52.5 ppm, respectively. There should be some other arsenic species in the sediment samples in addition to ionically bound As and strongly adsorbed As (such as As coprecipitated with amorphous Fe oxyhydroxides), since the total As concentration of each sample is evidently larger than the sum of ionically bound As and strongly adsorbed As. We calculated the ratio of the sum of ionically bound As and strongly adsorbed As to total As, the results being between 26.8% and 84.3% (the average ratio is 58.6%). It means that the observed arsenic in sediments is mainly from geothermal wastewater source (we think that ionically bound As and strongly adsorbed As in riverbed sediments come totally from adsorption of arsenic from river waters).

To delineate the variations of ionically bound As, strongly adsorbed As, and total As in the riverbed sediments of the Zangbo River, the concentrations of these arsenic species in the samples collected along the flow direction of the river in 2007 were plotted in Figure 2. It can be clearly seen from Figure 2 that the samples R2-07 located upstream of the wastewater draining exit of the first power plant have low concentrations of ionically bound As, strongly adsorbed As, and total As, indicating that it is free from contamination induced by the power plant wastewaters. By contrast, the concentrations of arsenic species in the sample R3-07 collected at the nearest downstream of the wastewater draining exit are markedly higher than those of the sample R2-07, showing the evident effect of geothermal wastewater drainage on riverbed sediments. In other words, the wastewaters from the first geothermal power plant with high arsenic concentration (up to 2.68 mg/L) are drained immediately into the Zangbo River, increasing the arsenic concentration in river waters, which in turn accelerates the adsorption of arsenic on riverbed sediments. Similarly, it can be noticed that the samples R5-07 and R7-07 collected from two streams where the geothermal wastewaters from the second power plant are drained, have very high concentrations of ionically bound As, strongly adsorbed As, and total As, which means that there has been evident migration of arsenic from wastewaters to stream waters and then to streambed sediments. Under the mixing effect of these two streams that serve as the wastewater drainage channels of the second power plant, the samples R6-07 and R8-07 located just in the conjunctions between the Zangbo River and these two channels also have comparatively higher concentrations of ionically bound As, strongly adsorbed As, and total As, compared with those samples collected at the downstream of them. It is also interesting to note that the sample R1-07 have comparatively higher arsenic species concentrations than R2-07, meaning that there may be other arsenic source for this sample. According to our field investigation, there are some low-temperature warm springs in the upstream of the Zangbo River. Although we did not sample these warm springs due to limited field working time, it can be speculated that they may be the source of arsenic in the sediment sample R1-07.

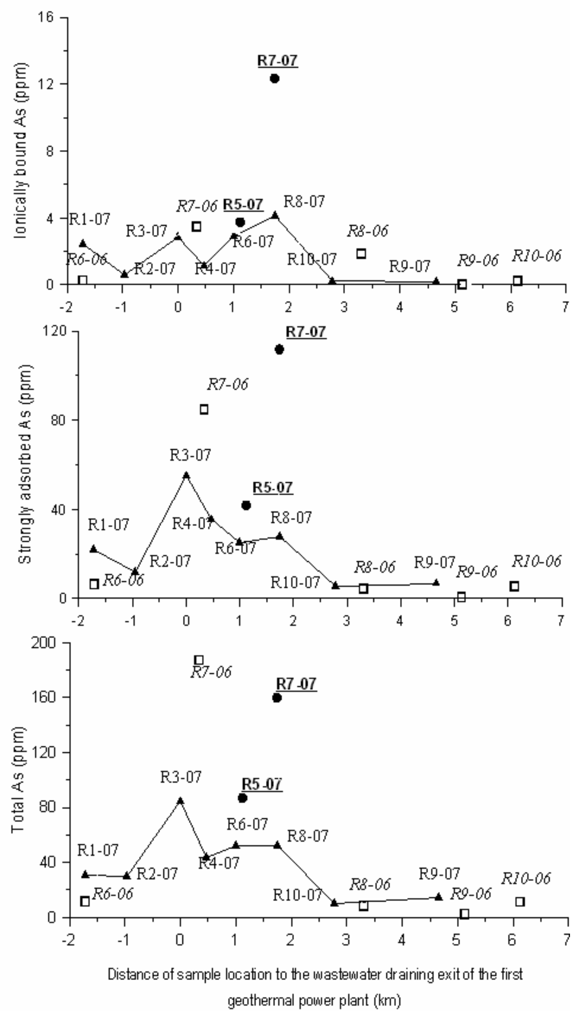

Figure 2: Variations of ionically bound As, strongly adsorbed As, and total As in all sediment samples. Legends: ▲, samples collected along the Zangbo River in 2007; ●, samples collected in the two wastewater drainage channels of the second geothermal power plant in 2007; □, samples collected along the Zangbo River in 2006.

Five riverbed sediment samples collected along the Zangbo River in 2006 were also plotted on the Figure 2. It is worth noting that the concentrations of ionically bound As, strongly adsorbed As, and total As in most samples of 2006 match well with the curves in Figure 2 delineating the variations of arsenic species in the samples of 2007. However, the concentrations of ionically bound As, strongly adsorbed As, and total As in the sample R7-06 are evidently higher than those in R3-07, although these two samples were collected almost in the same site. During our field investigations, it was observed that the rainfall in the study area in August of 2007 is much higher than that in June of 2006, and as a result, the runoff of the Zangbo River during our second sampling is also higher than that during first sampling. Therefore, the larger runoff may result in the desorption of ionically bound As and strongly adsorbed As from riverbed sediments, which in turn lowers the concentrations of arsenic species in riverbed sediments at the nearest downstream of the wastewater draining exit of the first power plant.

4. CONCLUSION

In conclusion, the riverbed sediments of the Zangbo River can be regarded as one of the sinks of arsenic from geothermal wastewaters. The migration of arsenic from river waters to riverbed sediments can facilitate the decrease of arsenic concentration in the Zangbo River waters, which is favorable for reducing the threat of arsenic in the river waters on the health of local residents.

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