IOP Conf. Series: Earth and Environmental Science **146** (2018) 012052 doi:10.1088/1755-1315/146/1/012052

Occurrence and Distribution of Arsenic in Water and Soil at Inland-Arid/Semi-Arid Basin

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Abstract. Hetao Basin, an inland-arid/semi-arid basin, is well known for the widely distribution of high arsenic groundwater and the serious local arseniasis causing by drinking high arsenic groundwater. Shallow groundwater in the basin generally occurs in the Quaternary alluvial, alluvial-pluvial, and fluvial-lacustrine aquifers, which are unconfined or leaky-confined. In this study, soil samples, surface water and groundwater samples were taken from Hetao Basin to analyse the occurrence and the distribution of arsenic in water and soil environments in this inland-arid/semi-arid basin. This study will provide a scientific basis for protect the safety of water supply in high arsenic groundwater areas.

1. Introduction

Hetao Basin (HB) is located in the west of Inner Mongolia with an area of about 13,000 km^2, and it extends north to the foot of Yin Mountains, south to the scarp in the northern edge of Ordos Loop, west to Ulanbuhe Desert, and east to the piedmont hills of Manhan and Lingel Mountains (Figure 1). It covers 500 km from east to west and 20-90 km from south to north, with an area of gently from southwest to northeast. Several polymetallic (Fe, Cu and Zn) sulfide ores are distributed along Yin Mountains. Among them, two large-scale deposits Tanyaokou and Dongshengmiao in the north of Hangjinhouqi have been mined since the 1970s. HB has a long history of using Yellow River as the water resource for irrigation purposes since the Qin Dynasty.

The climate is continental arid and semi-arid, with an average annual precipitation of 150-400 mm decreasing from east to west and evaporation of 2,000-2,600 mm. In this area, the precipitation from June to August accounts for 60-80% of annual precipitation. The Yellow River, flowing through HB with a length of approximately 350 km and an average annual runoff of 20-35 cubic meters, has been used as an water source for the irrigation purpose since Qin Dynasty at 221 BC and as an important agricultural food production base [1].

Shallow groundwater at HB generally occurs in the unconfined or leaky-confined Quaternary alluvial, alluvial-pluvial, and fluvial-lacustrine aquifers [2]. The aquifer sediments are mainly composed of alluvial arenaceour mud and sand, and lacustrine muddy clay and arenaceour mud which are rich in organic matter.

Groundwater is recharged by vertically infiltrating meteoric water in the plain, the lateral flow of fracture water from bedrock along the front of the Yin Mountains, irrigation return flow, surface water runoff and leakage from the Yellow River. Groundwater flow is generally slow in this area and is affected by geological structure, the gentle surface topography with a low hydraulic gradient, and the low hydraulic conductivity of fine-grained sediments. In general, two flow regimes can be detected in HB: (1) flow in the alluvial apron in front of the Yin Mountains from north to south and (2) flow inside the plain along the southwest-northeast direction, flowing finally to the east. Shallow groundwater is discharged mainly via evapotranspiration and artificial extraction, finally to Wuliangsuhai Lake in the east of HB.

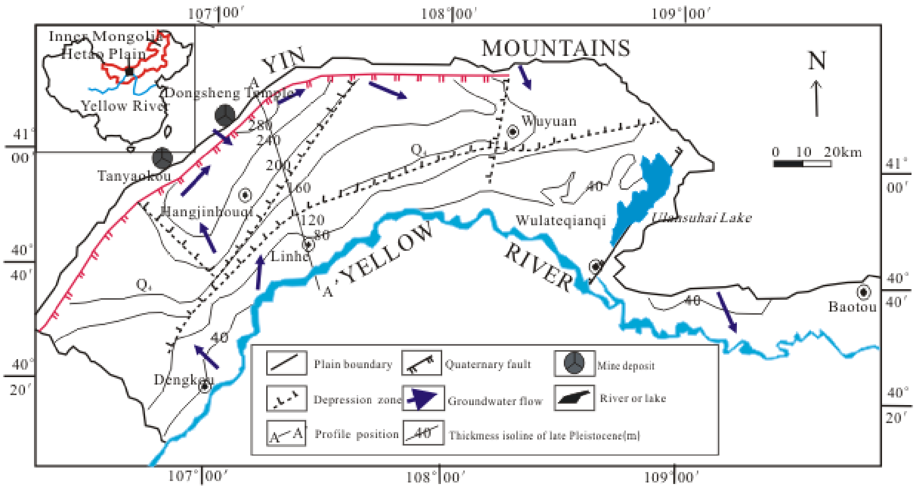

Figure 1. Location of HB, Inner Mongolia (modified from [3])

2. Materials and methods

2.1. Site description

Hangjinhouqi County, located in the western part of the HB, is selected as the study area. It has been concerned for over two decades because of the most serious endemic arsenicosis in Inner Mongolia province, as a representative for northern China. Groundwater with high levels of arsenic (As), TDS or high levels of F is the only source of potable water for about 50% of local residents in rural areas in the last several years. To date, the population of arsenicosis patients has exceeded 1100 people. At the margin of the Yin Mountains in the north of Hangjinhouqi county, there are two large-scale polymetallic (S, Pb, Zn) sulfide ore deposis, which have been mined since 1970s. Hangjinhouqi county is also a part of Hetao Irrigation Area. The vast majority of agricultural irrigation water in this study area is supplied by these four diversion channels: the main irrigation channel, the Ula Rriver, the Yangjia river, and the Huangji channel. There are also four drainage channels: the main drainage channel and drainage channels labeled simply No.1, No.2 and, No.3 drainage channels. The main drainage channel is located in the north of Hangjinhouqi County, which is the lowest place in the county. Thus, all the irrigation return flows, meteoric water, floods from the Yin Mountains front and residual water, the precipitation, the piedmont flood, the seepage, the industrial and domestic wastewater flow into the main drainage channel.

2.2. Sampling and analysis

In order to get a general knowledge of As occurrence and distribution in environment at Hangjinhouqi county, soil samples, borehole sediment samples, surface water samples and groundwater samples were collected for chemical analysis. Subsoil samples were collected from abandoned irrigation channels, abandoned drainage channels and farmlands, with different depth intervals (0-20, 20-40, 40-60, 60-80, 80-100 cm). River sediment samples were collected from irrigation channels and drainage channels. Two boreholes (TYM and TYS) were dug in low-As areas and the other two (HF and SH) were in high-As areas. And data of boreholes TYS, HF and SH were cited from Deng's publication [4].

All soil and sediment samples were taken in clean aluminum boxes and sealed by airtight strips and were stored in a refrigerator until processed within 7 days.Sediment samples and soil samples were air-dried in the dark at room temperature, crushed in an agate mortar, and the passed through a 100-gauge mesh. 0.5 g of dry samples was initially digested with 9 ml of concentrated HNO_3, 2 ml of $HClO_4$ and 3 ml of HF at 180℃ for 24 hours. Then the solution was evaporated to dryness and 50 ml of 2% (V/V) HNO_3 was added prior to analysis. The As contents were measured by hydride generation atomic fluorescence spectrometry (HG-AFS) (AFS-820; Titan Instruments, Beijing, China).

Groundwater samples were collected after wells were pumped for approximately around 10 minutes. Samples were firstly filtered (<0.45μ m) and stored in 50 ml acid-washed HDPE bottles and acidified by ultra-pure HCl for total dissolved As analysis. All samples were kept at 4℃ and total As concentrations measured by HG-AFS within 7 days. As speciation separation was conducted in the field. Water samples were firstly filtered using 0.45 μm membrane filters (Whatman) to to separate particulate As and soluble As, then passed through silica-based strong anion-exchange cartridges (Supelco) to separate arsenite and arsenate species.

3. Results and discussion

3.1. As in soils and sediments

Table 1 shows the As, TOC and TP contents in soils and sediments and pH of samples. The national soil background level of As is 11.2 μg/g, while the background level in HB is 7.5 μg/g. As contents in abandoned irrigation channels range from 7.57 μg/g to 19.86 μg/g with an average of 10.26 μg/g, in abandoned drainage channels from 6.58 μg/g to 20.12 μg/g with an average of 13.06 μg/g, in farmland from 8.83 μg/g to 22.81 μg/g with an average of 15.06 μg/g. As in most of the subsoil samples is above the background value. The highest average content of As occurs in farmland, while the lowest value occurs in abandoned irrigation channel. As contents in river sediment from drainage channel are higher than from irrigation channel. Compare with low-As area where As contents ranging between 3.04 μg/g and 26.43 μg/g with an average of 12.95 μg/g, borehole sediments in high-As area have higher As contents between 6.80 μg/g and 58.53 μg/g with an average of 16.45 μg/g.

The correlation coefficients between As contents and other elements in soils and sediments were analysed. Lithogenic metals such as Ca and Co show a high correlation with As. The strong positive correlation between As and Fe, Mn, TOC at level of 0.01, which is also observed in sediments from SH borehole [4], suggests that these components are of importance for enrichment of As in soils and sediments. The good positive correlation between As and Si indicates that As is possible bound to silica colloids which was also evidenced using Nuclear Magnetic Resonance (NMR), X-ray Absorption (XAS) and micro X-ray Fluorescence (μXRF) [5].

A total of 26 soil and sediment samples were tested with sequential chemical extractions to differentiate pools of solid phase associated As and adsorbed and coprecipitated As (Figure 2). Subsoil samples contains three groups: the profile S1, S5, and S9 were dug from abandoned Laoxi irrigation channel, from an abandoned tributary of the second drainage channel, and from a farmland in high-As area, respectively, to get subsoil samples with a depth interval of 20 cm under the ground surface. River sediment sample of R2 were from an irrigation channel, while R6, R7, and R8 were from drainage channels. Borehole sediments of TYM were from low-As area. For the all 26 samples, residual and Fe/Mn oxide-bound As are the dominated fractions, accounting for over 50% of the total As. Water-soluble As contents ranges from 0.045 mg/kg to 1.326 mg/kg, and have a tiny percentage of total As. Exchangeable As contents are generally closed to carbonate-bound As contents in most samples, with exception in S5-6, S9-1, and river sediments. High As contents generally corresponded to high Fe/Mn oxide-bound As and organic matter/sulfide-bound As, indicating the affinity of As to Fe/Mn minerals, organic matter, and sulfide. Fe/Mn oxide-bound As and organic matter/sulfide-bound As are the major active As form in these samples.

3.2. As in surface water

As concentrations in irrigation channel water range from 6.2 μg/L to 17.1 μg/L with an average of 8.5 μg/L, while in drainage channel water from 5.9 μg/L to 25.3 μg/L with an average of 15.5 μg/L. The major irrigation channel, Yangjiahe River and the middle reach of Huangjin irrigation channel have As concentrations below 10 μg/L, except for the low reach of Huangjin irrigation channel in Shanba town containing 17.1 μg/L of As.

Table 1. Summary of As, TOC and TP contents in soils and sediments and pH of samples

	As (μg/g)		pH		TOC (%)		TP (μg/g)	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Subsoil								
Abandoned irrigation channel	7.57-19.86	10.26	8.17-8.67	8.45	0.08-0.30	0.2	335.68-641.84	453.79
Abandoned drainage channel	6.58-20.12	13.06	7.84-8.83	8.35	0.08-1.47	0.33	355.71-756.85	512.92
Farmland	8.83-22.81	15.06	8.49-8.80	8.65	0.08-0.52	0.26	251.89-658.25	455.64
River sediment								
Irrigation channel	7.58-7.69	7.64	8.70-9.18	8.94	0.04-0.10	0.07	363.24-490.70	426.97
Drainage channel	14.97-27.50	19.10	ND		ND		ND	
Borehole sediment								
Low-As area	3.04-26.43	12.95	8.41-9.73	8.89	BDL-2.00	1.25	122.77-889.26	501.97
High-As area	6.80-58.53	16.45	ND		ND		ND	

BLD: Below detection limit
ND: No detected

As concentrations in drainage channel water range from 5.9 μg/L to25.3 μg/L with an average of 15.5 μg/L. The highest concentration occurs at the third drainage channel, while the lowest concentration occurs at the major drainage channel near Hongfeng village.

One surface runoff sample collected from the Yin mountains front contains 11.2 μg/L of As. The rainwater collected in August 2011 contains 8.8 μg/L of As. As concentration in rainwater at HB is 0.28 μg/L in July 2009 [2]. Based on the results of 35 rainwater samples in Asia, As is found below 10 μg/L.

3.3. As in groundwater

In Hangjinhouqi county, dissolved As concentrations in groundwater are in the range of 0.5 μg/L to 720.7 μg/L with an average of 105.9 μg/L. 66.88% of (103) groundwater samples exceed the standard for allowable As concentration 10 μg/L in drinking water.

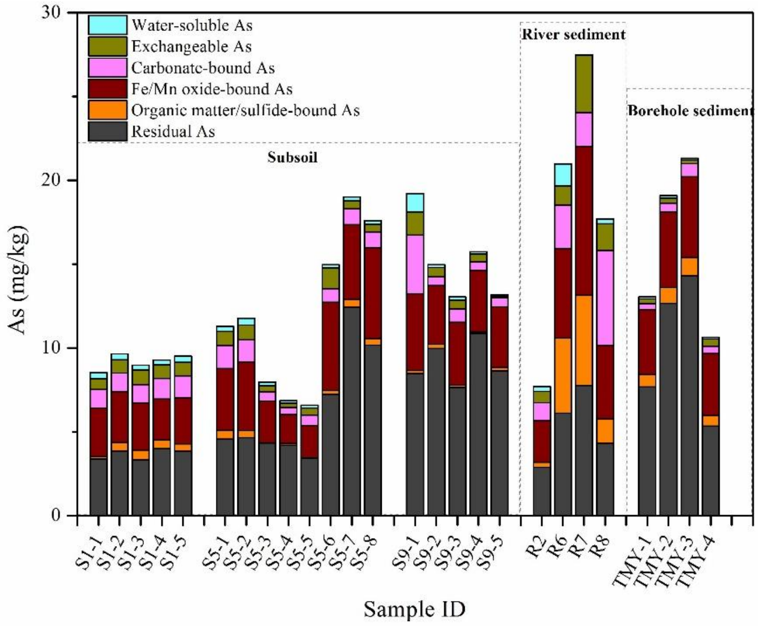

Figure 2. As forms (including water-soluble As, exchangeable As, carbonate-bound As, Fe/Mnoxide-bound As, organic matter/sulfide-bound As, and residual As) in subsoil from different depth intervals (0-20, 20-40, 40-60, 60-80, 80-100, 100-120, 120-140, and 140-160 cm), river sediment, and low-As borehole sediment from Hangjinhouqi county

All the samples were taken from wells with depths between 3 m and 80 m. The vertical profile of As clearly shows that high As concentrations were mainly observed from depth between 10 m and 40 m (Figure 3). The shallow groundwater samples from wells with depths less than 10 m had low As concentrations (less than 10 μg/L or closed to 10 μg/L). Those groundwater samples from wells with depths more than 40 m had As concentration less than 50 μg/L, except for one sample collected from a 80-meter-deep well with a As concentration of 140.2 μg/L. The highest As concentration in shallow groundwater is 720.7 μg/L with a well depth of 27 m.

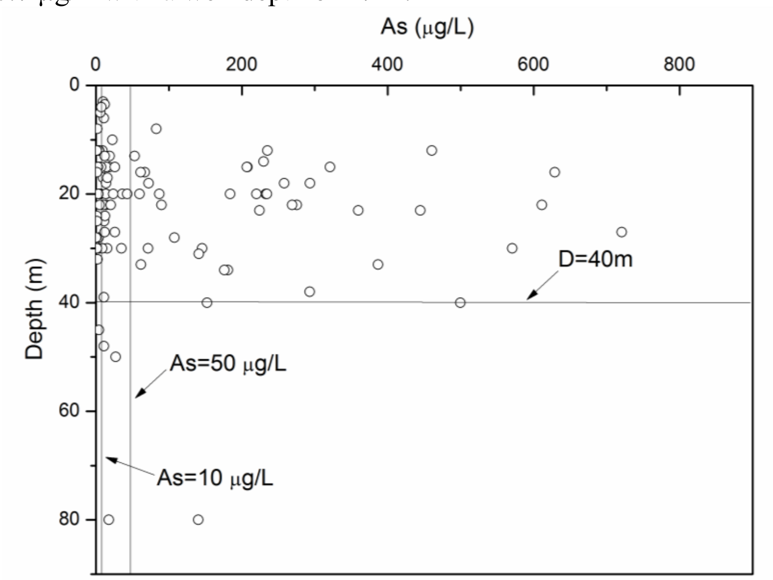

Figure 3. Depth distribution of As concentration in groundwater from groundwater at Hangjinhouqi county

As concentrations in groundwater varied in different districts of the study area. In the southern part of Hangjinhouqi county where groundwater mainly receives recharge from the Yellow River and has good runoff conditions, groundwater had low As concentrations <10 μg/L, or between 10 μg/L and 50 μg/L. In the center district, groundwater generally had As concentrations below 100 μg/L. High-As groundwater is distributed in the north of Hanjinghouqi county along the Yin Mountains where the groundwater flow is sluggish. This high-As district, is also a mosaic transition zone between The polymetallic sulfide mining area and the irrigation area. Groundwater in this district receives the recharge from the Yin Mountains front, as well as the seasonal recharge from the irrigation water and irrigation return in the main drainage channel.

4. Conclusion

As in most of the subsoil samples is above the background value. The highest average content of As occurs in farmland, while the lowest value occurs in abandoned irrigation channel. Compare with low-As area where As contents ranging between 3.04 μg/g and 26.43 μg/g with an average of 12.95 μg/g, borehole sediments in high-As area have higher As contents between 6.80 μg/g and 58.53 μg/g with an average of 16.45 μg/g. As concentrations in irrigation channel water range from 6.2 μg/L to 17.1 μg/L with an average of 8.5 μg/L, while in drainage channel water from 5.9 μg/L to 25.3 μg/L with an average of 15.5 μg/L. The major irrigation channel, Yangjiahe River and the middle reach of Huangjin irrigation channel have As concentrations below 10 μg/L, except for the low reach of Huangjin irrigation channel in Shanba town containing 17.1 μg/L of As. In Hangjinhouqi county, dissolved As concentrations in groundwater are in the range of 0.5 μg/L to 720.7 μg/L with an average of 105.9 μg/L. 66.88% of (103) groundwater samples exceed the standard for allowable As concentration 10 μg/L in drinking water. The vertical profile of As clearly shows that high As concentrations were mainly observed from depth between 10 m and 40 m. The shallow groundwater samples from wells with depths less than 10 m had low As concentrations (less than 10 μg/L or closed to 10 μg/L). Those groundwater samples from wells with depths more than 40 m had As concentration less than 50 μg/L, except for one sample collected from a 80-meter-deep well with a As concentration of 140.2 μg/L. The highest As concentration in shallow groundwater is 720.7 μg/L with a well depth of 27 m.

Acknowledgments

Authors wish to acknowledge the financial support by International Atomic Energy Agency Coordinated Research Project （IAEA No. 21122）, Open Fund of Jiangxi Key Laboratory for Mass Spectrometry and Instrumentation, East China University of Technology (No. JXMS2017016) and Water Resources and Water Environment Research Center Fund of Water Resources Ministry in China (No. ZXKT201709).

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