Hydrogeological and geochemical comparison of high and low arsenic groundwaters in the Hetao Basin, Inner Mongolia

H.Y. Wang

Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

ABSTRACT: For deeply understanding the arsenic mobilization mechanisms of groundwater in Hetao Basin of Inner Mongolia, sediments and groundwater samples from two multi-level wells (up to 80 m) were analyzed. The results showed that the sediment As content from well with high As concentration (K1) is higher than the well with low As concentration groundwater (K2), with the average As concentrations 14.7 and 12.8 mg kg⁻¹ respectively. Interestingly, we found a gray-black peat layer (around 28 m) from the K2, with arsenic concentration 322 mg kg⁻¹, while the TOC content and TS contents are up to 9.6% and 1.8%, respectively. The pyrite also was found in this layer. We conclude that the organic matter triggers the formation of arsenic-sequestering sulphides under strongly reducing conditions, therefore immobilization of As into the sediments. By bonding arsenic in this way, the peat layer occurred in the aquifer plays an active role for arsenic immobilization into the sediments.

1 INTRODUCTION

The Hetao Basin in the Inner Mongolia is one of most serious As-polluted area in China (Guo *et al.*, 2014; Liu *et al.*, 2017). Groundwater with high As concentration (up to 879 µg L⁻¹) has been widely found in the Hetao Basin, with 76000 people exposed in 35 villages in 2002 (Liu *et al.*, 2017).

For better understanding the mechanisms of As mobilization, we drilled two boreholes up to 80 m in Hangjinhoujin, one countryside highly affected by As pollution. The sediments from different layers were analyzed based on mineralogy and chemistry characters. And the relevance was established between the sediments property and groundwater As concentration.

2 METHODS

2.1 Study area

The Hetao Basin is located in between Yellow river to the south and Langshan to the north. Lacustrine deposition and frequent channel changes caused the patchy sediments distribution and allowed organic matter to accumulate in the sediments during Pleistocene and Holocene period. Hangjinhouqi country located in the west of Hetao basin is one of the serious arsenic-affected areas where the groundwater was mainly used for irrigation system.

2.2 Sediments characterization

Two boreholes up to 80 m were drilled at the Hangjinhouqi in October of 2015. The XRF analysis was used to determine the mineral phases and major chemical components. The total carbon components (TC) and

TS as well as organic matter (TOC) were qualified using carbon-water analyzer. The EC (electric conductivity) value of soluble contents and pH values of sediments were also measured by method of solid-to-liquid ratio of 1:5.

2.3 Groundwater sampling and analysis

After sediment sampling, the multi-level wells were installed. The water was pumped from the different depth. Groundwater parameters including temperature (T), pH, redox potential (ORP), electrical conductivity (EC) were measured in the field. The major cations including As and anions were measured by ICP-MS and ICP-OES respectively.

3 RESULTS AND DISCUSSION

3.1 Sediment geochemistry

The average sediment grain sizes from K2 borehole are larger than K1, while the medium-coarse sands distribute in 35–40 m and 51–60 m from K2 borehole, they are rarely found in K1. Compared with K1, clay layers are also widely distributed in K2 with yellow-brown layers found in the depth around 16 m, 26 m, 41 m, 51 m, 59 m, 65 m respectively, while only two clay layers appeared in K1 with the depth around 3 m above the aquifer, and 40 m, respectively.

The sediment As contents ranged from 5.8 to 28.9 mg kg⁻¹ (Table 1) with higher As contents of clay samples. Therefore, the clay layers intersected in the aquifers can be a major As sink or source. The As contents are well correlated with Fe contents in the sediments, rather than TOC and TS. So the As occurred in the aquifer are mostly from the

Table 1. Chemical compositions of sediment samples collected from two boreholes in the western Hetao basin a: K1, b: K2 (except one sample with As content up to 322 mg kg⁻¹). a:

Value range	Fe ₂ O ₃ (wt%)	MnO (wt%)	As (mg kg ⁻¹)	TOC (%)	TIC (%)	TS (mg kg ⁻¹)
Maximum	7.15	0.120	40.9	0.60	2.15	5125
75% Q	5.76	0.092	21.0	0.37	1.64	512
Median	3.39	0.047	12.1	0.13	0.97	287
25% Q	2.14	0.034	7.71	0.06	0.63	231
Minimum	1.61	0.023	5.82	0.04	0.32	140
Average	3.80	0.060	14.7	0.20	1.14	573
R ² _{Fe}	—	0.93	0.75	0.61	0.80	0.0052
R ² _{As}	—	0.61	—	0.35	0.40	0.0375

b:

Maximum	6.85	0.109	28.9	0.90	1.92	5438
75% Q	5.17	0.083	16.1	0.47	1.74	685
Median	3.59	0.056	11.9	0.20	1.16	322
25% Q	2.16	0.029	6.59	0.06	0.53	226
Minimum	1.68	0.025	5.03	0.05	0.31	179
Average	3.69	0.058	12.8	0.2	1.10	724
R ² _{Fe}	—	0.97	0.74	0.48	0.7	0.16
R ² _{As}	—	0.66	—	0.50	0.6	0.35

dissolution of Fe/Mn (hydro) oxides or the Fe(Mn) oxides-TOC-As complexes.

The average As content (14.7 mg kg⁻¹) in the K1 borehole is higher than in the K2 (12.7 mg kg⁻¹) (Table 1). It may be an important reason for higher groundwater As concentration from K1 well.

Interestingly, we found a gray-black peat layer in the K2 borehole. The deep sand layer contains trees and plants debris extending from 25.8 to 28.4 m with the As and TOC contents up to 322 mg kg⁻¹ and 9.6% respectively. XRD spectra was used to investigate the mineral compositions, revealing that the pyrite minerals appeared in this layer. Under reducing conditions, the S-enriched peat can implicate as a fuel for reductive dissolution of arsenic-bearing iron (hydro) oxides, then accelerate the formation of arsenic-contained pyrite as a result of sulfides reacting with the Fe (II).

3.2 Soluble salts in the sediments

Generally, the clay and silt samples exhibited higher salinity than the sand. However, the sand layers in the depth of around 80 m in K1, 28 m and 69 m in K2 released high contents of salts due to the high TOC contents (Fig. 1a). The sample EC values near the land surface from K1 are much higher than from K2, indicating that the groundwater from K1 well experienced long time evaporation and caused the salts accumulation in the surface sediments. Contrasting with K1, the sediments from K2 experienced long-term flushing history with low EC values appearing at different aquifer sediments.

Compared with higher sediment As concentration from K1 borehole, the sediments from K2 have higher pH value (Fig. 1a). It may be due to that at alkaline

Figure 1. (a) EC value and pH of sediments varies with depth, (b) As concentrations of groundwater and sediments varies with dept.

conditions, dissolved Fe concentrations did not significantly increase upon reduction. Furthermore, the presence of soluble organics under alkaline conditions and the formation of iron oxyhydroxides-organic matter complexes could have retarded Fe reduction and the release of As into solution.

3.3 Hydrogeochemistry

The groundwater from K2 well showed higher pH, consisting with higher pH in the sediments. The total dissolved solids (TDS) range from 449 to 3136 mg L⁻¹, and decline with the depth. The groundwater from K1 well experienced long-time water-rock interaction or evaporation process with higher EC value. The groundwater samples from K1 well are mostly Na-Cl-SO₄ or Na-SO₄-Cl type, while samples from K2 well are mostly Na (Ca)-HCO₃-SO₄ type.

The ORP values of both wells are similar under anoxic conditions except the depth of 15–16 m in K2 well. The groundwater As concentrations from different depths of K2 well are lower than 50 µg L⁻¹, and increased with depth (Fig. 1b). Even though the sediment As content in the depth of 28 m from K2 borehole is up to 322 mg L⁻¹, the As concentration in the groundwater according to this depth is lower than 10 µg L⁻¹. Therefore, we conclude that the peat layers accelerate the As immobilization into the sediments.

The groundwater As concentrations in K1 vary with the sediment As contents. The As concentration in the depth of 42.5 m is 174 µg L⁻¹ while the As content in the upper clay sediment is up to 25 mg kg⁻¹ (Fig. 1b). Under reducing conditions, the DOC released from clay layers above this aquifer may afford the electrons for release of Fe (hydro) oxides.

REFERENCES

Guo, H.M., Wen, D.G., Liu, Z.Y., Jia, Y.F. & Guo, Q. 2014. A review of high arsenic groundwater in mainland and Taiwan, China: distribution, characteristics and geochemical processes. *Appl. Geochem.* 41: 196–217.

Liu, N.J., Deng, Y.M. & Wang, Y. 2017. Arsenic, iron and organic matter in quaternary aquifer sediments from western Hetao Basin, Inner Mongolia. *J. Earth Sci.* 28: 473–483.