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Influences of sediment characteristics and land utilization on the behavior of groundwater arsenic (As) in the Kuitun River basin

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ABSTRACT

To better understand the formation and migration of high-arsenic groundwater, the influences of geochemical characteristics of sediments, and land utilization must be further studied. To better understand these dynamics, 76 groundwater samples from different scales of the landscape (alluvial–proluvial plain, downstream flood irrigation zone and downstream drip irrigation zone) were collected and tested to analyze the contents of their major and trace components. Forty-two sediment samples from two boreholes were collected and different variables such as particle size distribution, chemical composition, and concentrations of weakly (*S*1) and strongly (*S*2) bound As were tested for physiochemical index analysis. Results showed that high-As groundwater (As concentration >10 μg/L) was mainly distributed at depths of 20–36 m; the groundwater in the alluvial–proluvial plain had a generally low As concentration with an average concentration of 9.6 μg/L; and the groundwater in the flood irrigation zone and that in the drip irrigation zone had relatively high As concentrations with average concentrations of 36.0 and 151.45 μg/L, respectively. In the sediments, As content was positively correlated with Fe and Mn content, and its distribution was controlled by hydrodynamic conditions and lithology, with clay having a relatively high As content. The competitive adsorption by PO_4^{3-} promoted the release of As in the sediments. As concentration in groundwater in the drip irrigation zone (known for growing cotton using drip irrigation, which demands high-phosphate fertilizer) was higher than that in the groundwater in flood irrigation zone (known for vegetable agriculture using flood irrigation, which demands high-potash fertilizer), suggesting that land use patterns have a significant influence on the distribution and migration of As.

Keywords: The Kuitun River basin; Sediment; As; Partition coefficient values; Land utilization

1. Introduction

Naturally occurring groundwater with high levels of arsenic (high-As groundwater) poses one of the most severe environmental geological problems, and threatens the physical health of millions worldwide [1]. In China, high-As groundwater is found in two types of regions: arid inland basins, such as the Junggar Basin in Xinjiang, the Datong Basin in Shanxi, the Hohhot Basin, and the Hetao Basin in Inner Mongolia, the Songnen Basin in Jilin, and the Yinchuan Basin in Ningxia, and river deltas, such as the Pearl River Delta, the Yangtze River Delta, and the Jianghan Plain [2]. Long-term exposure to high-As groundwater through drinking or physical contact causes As poisoning, which leads to diseases such as skin, bladder, liver, and lung cancer.

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A number of studies have investigated the causes for As accumulation in groundwater. Postma et al. [3] theorized that the enrichment of As was caused by the reductive dissolution of arsenious minerals. Mukherjee et al. [4] revealed that As-rich minerals were related to the Holocene alluvial sediments of Quaternary deposit. Drahotad et al. [5] and Verma et al. [6] found that As-rich sediments were transported by rivers running through the Himalayas, leading to deposition of As in downstream basins and delta regions.

Microbes take advantage of the organic matter buried in sediments for their metabolic activities. Microbes reduce Fe^{3+} into Fe^{2+} to consume the oxygen bound arsenious Fe oxide to Fe hydroxides, which leads to the release of As. The migration and enrichment in groundwater system of As are controlled by many different factors such as redox conditions, pH value, presence of organic matter, and microbial activities [7]. In recent years, the importance of sediment properties in regulating the migration of As in groundwater systems through various processes, including changes in the flow and circulation of groundwater, local redox environment, and microbial activity. By investigating the shallow groundwater and sediments in southeastern Bangladesh, Hoque et al. [8] revealed that soil texture affects whether As is released into groundwater. By studying the sediments in the high-As area of the Hetao region, Inner Mongolia, China, Gao et al. [9] concluded that the sedimentary environment and sediment characteristics influenced the enrichment and migration of As in groundwater. A study by Cao et al. [10] on the high-As area of the Yinchuan Plain showed that sediment properties and land use patterns significantly influenced the distribution and migration of As. Thus, it is important to ascertain how land utilization and the geochemical characteristics of sediments influence the formation and migration of high-As groundwater is urgent for regions high in As.

Kuitun in Xinjiang was the first region that was significantly affected by large-area endemic As poisoning in mainland China [3]. Thirty years after the water system was improved, the residents living in Kuitun still have a relatively high *in vivo* As level [11]. The high-As groundwater in this region is mainly distributed on the fine soil plain of the basin. To this point, there have been few reports on the mechanism by which groundwater migration and enrichment of high arsenic in this area occurs. On the basis of ascertaining the distribution characteristics of the high-As groundwater in the Kuitun River Basin, this paper examined Shiqiao Township (known for growing cotton using drip irrigation, which demands high-phosphate fertilizer) and Chepaizi Town (known for vegetable agriculture using flood irrigation, which demands high-potash fertilizer) in the downstream area of the Kuitun River Basin as the areas to drill boreholes and sample sediments. The two areas were then compared with respect to sediment properties, As a distribution, and the existing As a state to reveal the effects of sediment particle size distribution. By exploring the relationship between the hydraulic characteristics of aquifers and the existing states of As in the two areas, we found that the circulation of groundwater and the formation of high-As groundwater were correlated, and the existing As states contributed towards the formation of high-As groundwater. Overall, we provide insights into the migration and occurrence of As under two different land-use patterns.

2. Materials and methodology

2.1. Overview of the study area

The Kuitun River Basin is located on the northern slope (inclining to the west) of the Tianshan Mountains at the southern margin of the Junggar Basin, and borders on the Gurbantunggut Desert in the Junggar Basin in the north. Dominated by a northern temperate continental arid climate, this area has little annual precipitation but high annual evaporation [12]. The plain area of the basin consists of two parts: the piedmont proluvial gravelly inclined plain area, and the alluvial–lacustrine plain area. The former is a singular phreatic aquifer, and is dominated by pebble gravel and sandy pebble gravel in a lithological composition and is highly permeable. The latter has a groundwater burial depth of 60–75 m near the Wuyi Road. Below the groundwater spilling belt of downtown Kuitun, aquifer number gradually increases, and there the sediment between the aquifers is pebbly loam. There is also a gradual transition to multi-layered phreatic-confined aquifers [13]. The two sediment borehole sampling areas were both located downstream of the alluvial–lacustrine plain area, as shown in Fig. 1.

2.2. Sample collection and analysis

2.2.1. Groundwater sample collection and analysis

A total of 76 groups of groundwater samples were collected from the study area, including 19 groups from the Chepaizi flood irrigation zone (referred to as “the flood irrigation zone”), 16 groups from the Shiqiao drip irrigation zone (referred to as “the drip irrigation zone”), 33 groups from the alluvial–proluvial plain, four groups from Z1 (corresponding to sampling depths of 10, 18, 28, and 45 m), and four groups from Z2 (corresponding to sampling depths of 12, 20, 30, and 40 m; Fig. 1). Boreholes Z1 and Z2 were located in the Chepaizi and Shiqiao drip irrigation zones, respectively, with a uniform hole depth of 45 m. Before sampling, a pump was used to draw water for at least 15 min, and a portable water quality analyzer was used to determine the groundwater quality parameters at the time the samples were collected, including temperature, electrical conductivity (E_c), pH, and Eh value (oxidation-reduction potential). All the samples were screened via a 0.22 μm filter on site. A 1:1 HNO_3 solution was added until the pH < 2. After treatment, all samples were sealed, stored below 4°C, and submitted for testing.

2.2.2. Sediment sample collection and analysis

Boreholes Z1 and Z2 were drilled in the flood irrigation zone and the drip irrigation zone, respectively (Fig. 1). Twenty groups of sediment samples were collected from borehole Z1, and 22 groups from borehole Z2. The general rule was to collect one group of sediment samples every 3 m. When there was an abrupt change in lithology, sampling density was increased. During sampling, exterior mud was peeled off, and 500 g sediment cores were taken out and immediately wrapped with tinfoil. Samples were then placed in a blender bag, which was filled with nitrogen, sealed, stored

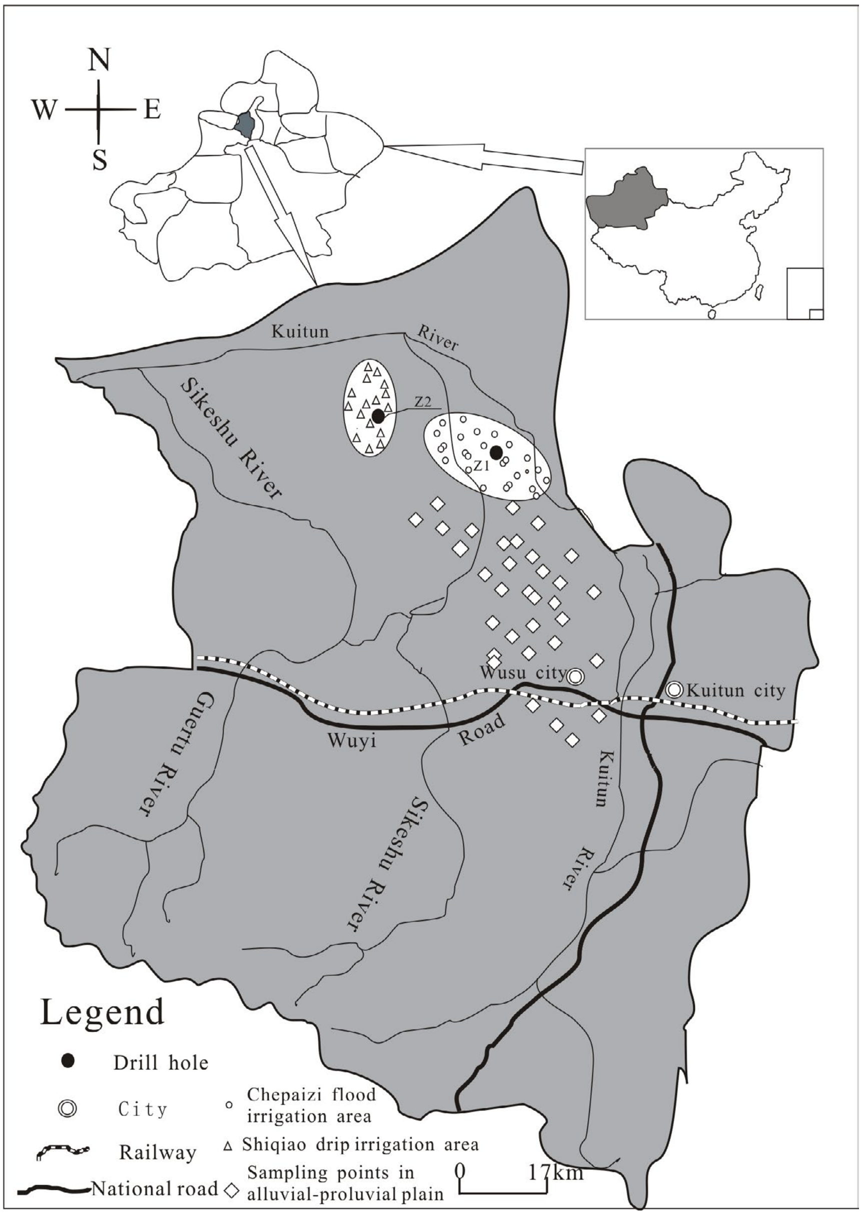


Fig. 1. Locations of study area and sampling sites.

at a low temperature, and later stored at –20°C. Testing and analysis were completed within 2 weeks.

After samples were treated, the chemical composition of the sediments was tested. Sediment samples were weighed to 100 g, air-dried, and homogenized in a bowl until samples were able to pass through a 200-mesh filter. After sample marking, sediment composition analysis was performed. To analyze elements such as As and Fe, it was necessary to first fully dissolve the samples with HCl, HF, and HNO_3, and then use an atomic absorption spectrometer to determine the composition.

The extraction of strongly and weakly bound. As from the sediments were conducted following Keon's method [14]. The specific extraction methods were as follows:

Weakly bound As (S1): At room temperature, 0.4 g sediment samples (frozen, dried, and uniformly ground) were placed into a 50 mL centrifuge tube, then 20 mL $MgCl_2$ (1 mol/L, pH = 8 after regulation) was added to extract As for 2 h. Samples were stirred without interruption in two replicates, and the extracts of the two replicates were loaded into the same bottle for analysis.

Strongly bound As (S2): At room temperature, the centrifugal residue left after *S*1 extraction was added to 20 mL NaH_2PO_4 (1 mol/L, pH = 5 after regulation), for two replicates. The time nodes for the two extractions were done at 16 and 24 h, and the extracts were transferred into the same bottle for analysis within 24 h. The sediment extraction experiment was performed in an anaerobic chamber, and all extracts were prepared with ultrapure water (having been denitrified for 2 h through nitrogen flushing).

A laser particle size analyzer was used to determine the particle size distribution of sediment samples, and

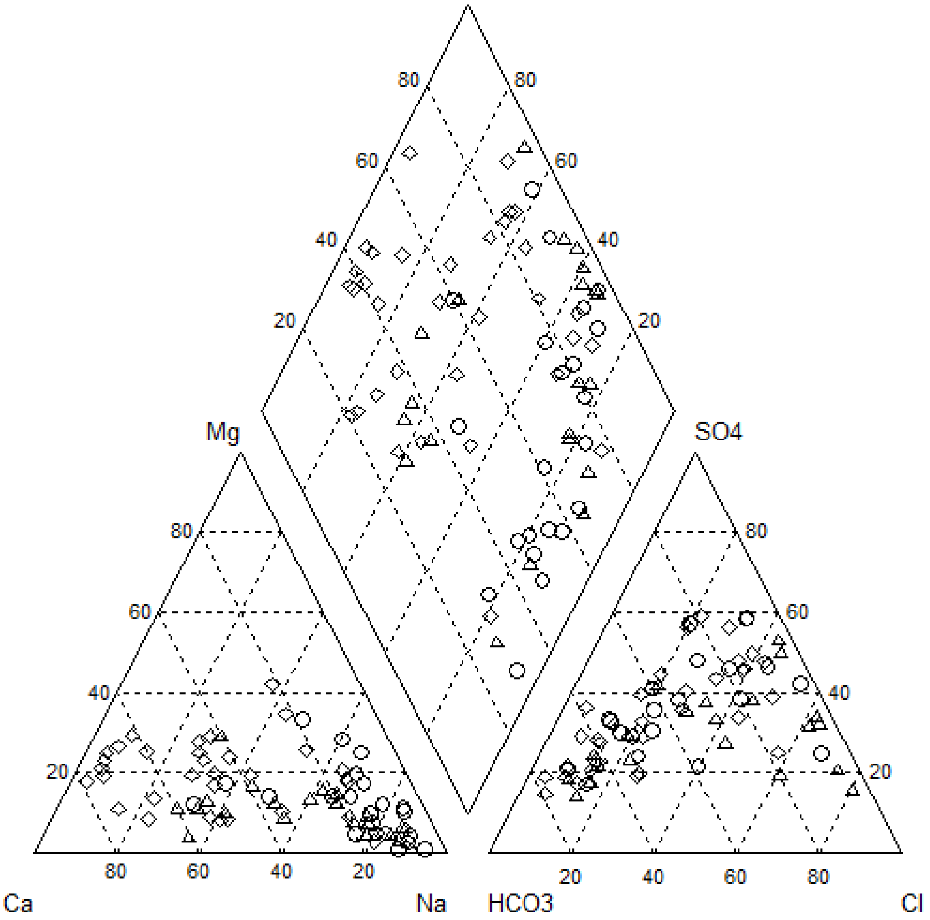


Fig. 2. Piper diagrams of groundwater from different zones in the study area.

these measurements were used to calculate the hydraulic conductivity coefficient of sediment samples.

3. Results and analysis

3.1. Hydrochemistry of groundwater

3.1.1. Basic hydrochemical characteristics

The pH ranges of the samples collected from the alluvial–proluvial plain, the flood irrigation zone, and the drip irrigation were 7.28–8.30 (7.83 on average), 7.40–8.91 (8.35 on average), and 7.42–8.96 (8.12 on average), respectively. These results indicated that the groundwater in the study area was in a weakly alkaline environment. Comparing the Piper trilinear nomograph of groundwater (Fig. 2) and various sampling sites, the primary hydrochemical type of the groundwater in the alluvial–proluvial plain was $HCO_3 \cdot SO_4$–Ca·Mg; the main hydrochemical types of the groundwater in the flood irrigation zone were $SO_4 \cdot Cl$–Na type and $HCO_3 \cdot SO_4$–Na type; and the primary hydrochemical type of the groundwater in the drip irrigation zone was $Cl \cdot SO_4$–Na·Ca type.

The groundwater from the drip irrigation zone had a higher concentration of Cl^- compared to the alluvial–proluvial plain and the flood irrigation zone. Specifically, the average Cl^- concentration in groundwater of the drip irrigation zone reached as high as 362.32 mg/L, while those of the alluvial–proluvial plain and the flood irrigation zone were 105.91 and 218.40 mg/L, respectively. The groundwater in the flood irrigation zone had a higher concentration of SO_4^{2-}, with a maximum value of 1,962.44 mg/L and average of 352.68 mg/L. In contrast, the alluvial–proluvial plain had lower levels of SO_4^{2-}, with an average of 200.79 mg/L. The anions in groundwater in the alluvial–proluvial plain were dominated by HCO_3^-, and its concentration range was 83.07–486.20 mg/L and an average concentration of 151.83 mg/L. The groundwater in the flood irrigation zone and in the drip irrigation zone had lower HCO_3^- concentrations with concentration ranges of 78.18–342.05 and 85.51–183.94 mg/L, respectively. In the alluvial–proluvial plain, the flood irrigation zone, and the drip irrigation zone, the average HPO_4^{3-} concentrations in groundwater were 0.14, 0.23, and 0.32 mg/L, respectively, the average Na^+ concentrations in groundwater were 92.24, 226.94, and 248.09 mg/L, respectively, and the average Ca^{2+} concentrations in groundwater were 62.15, 49.20, and 102.88 mg/L, respectively. These results highlight that the drip irrigation zone had higher levels of Na^+ and Ca^{2+} in the groundwater compared to the other two zones. Their average electrical conductivity (E_c) values were 740, 1,503, and 1,499 µs/cm, respectively, therefore groundwater salinity increased from the alluvial–proluvial plain to the downstream region of the Kuitun River Basin.

The Eh of groundwater showed some spatial variations. The groundwater samples collected from the alluvial–proluvial plain had an Eh range of –54–112 mV, and an average value of 21 mV; the Eh ranges of the groundwater samples collected from the flood irrigation zone and the drip irrigation zone were –160–81 (–15 on average) mV and –49–65 (–12 on average) mV, respectively. Clearly, compared to the flood irrigation zone and the drip irrigation zone, the alluvial–proluvial plain was in an environment more conducive to oxidation. In the three zones, the NO_3^- concentration ranges in groundwater were <0.05–40.25 (12.31 on average), <0.05–8.58 (2.29 on average), and <0.05–7.50 (1.05 on average) mg/L, respectively; and the NH_4^+ concentration ranges in groundwater were 0.05–1.23 (0.27 on average), 0.04–1.41 (0.30 on average), and 0.07–0.93 (0.41 on average) mg/L, respectively. Clearly, from the alluvial–proluvial plain to the downstream area of the Kuitun River Basin, the spatial variation trend of NO_3^- concentration and Eh both gradually declined, contrary to the trend presented by NH_4^+ concentration. The average total Fe concentrations of the three units were 0.21, 0.17, and 0.07 mg/L.

3.1.2. As distribution characteristics in groundwater

The groundwater in the alluvial–proluvial plain had a relatively low As concentration, and only five of the 33 groups of samples exceeded the class III water quality standard (10 μg/L) specified in the Standard for Groundwater Quality of China (GBBT 14848-2017). The As concentrations of the five groups were 33.7, 38.8, 43.6, 42.6, and 19.3 μg/L, respectively. The groundwater in the flood irrigation zone and that in the drip irrigation zone had generally high As concentrations. In the flood irrigation zone and the drip irrigation zone, more than 93.8% and 83.3% of samples had As concentrations of above 10 μg/L, respectively, where As concentration ranges were <0.01–95.6 and <0.01–132.6 μg/L, respectively. As concentration increased from the alluvial–proluvial plain to the downstream area of the Kuitun River Basin, while the As concentration in the drip irrigation zone was higher than in the flood irrigation zone. In the vertical direction, high-As groundwater was mainly distributed at depths of 20–36 m. The groundwater sample with the maximum As concentration of 132.6 μg/L was collected at a depth of 30 m. The groundwater samples collected from a depth of above 40 m had relatively low As content (uniformly lower than 50 μg/L). The results observed through multi-stage monitoring boreholes were consistent with the above vertical distribution patterns. In the *Z*1 monitoring hole, the As concentrations in groundwater at the depths of 10, 18, 28, and 45 m were 35.2, 24.3, 36.7, and 3.6 μg/L, respectively. In the *Z*2 monitoring hole, the As concentrations in groundwater at the depths of 12, 20, 30, and 40 m were 25.1, 7.5, 8.2, and 3.7 μg/L, respectively.

3.2. Geochemical characteristics of sediments

3.2.1. Particle size distribution and As content characteristics of sediments

According to the particle size distribution data measured by the laser particle size analyzer, the maps highlighting the distribution of particle size of the sediments collected from the two boreholes were generated (Figs. 3a and c). Depending on the particle size, the sediments were divided into four levels: (1) particle size <0.063 μm: clay or silty clay; (2) 0.063 < particle size < 200 μm: fine sand; (3) 200 < particle size < 630 μm: medium sand; and (4) particle size > 630 μm: coarse sand.

Overall, the average clay, fine sand and medium sand contents of *Z*1 borehole were 29.8%, 76.1%, and 93.7%, respectively. Clay content exceeded 90% in samples collected from depths of 0–3 and 12–15 m. The average clay, fine sand, and medium sand contents of the *Z*2 borehole were 28.9%, 77.2%, and 94.5%, respectively; at depths of 9–12 m, clay content exceeded 90%. In terms of sediment composition, there was no significant lithological difference between the two boreholes.

In *Z*1 borehole, the As content in the sediments ranged from 4.63–79.90 mg/kg (15.70 mg/kg on average). At the depth of 15 m, the As content reached its peak at 79.90 mg/kg and the clay content was 91.1% (Figs. 3a and b). *S*1 had an As content range of <0.01–0.39 mg/kg, and an average value of 0.12 mg/kg, and *S*2 had a content range of <0.01–5.00 mg/kg, and an average value of 0.89 mg/kg (Fig. 3d). In *Z*2 borehole, the As content in the sediments ranged from 6.21 to 31.32 mg/kg (11.2 mg/kg on average), and reached its peak at the depth of 12 m, where the clay content was 90.1% (Figs. 3e and f). *S*1 had a content range of <0.01–0.42 mg/kg, and an average value of 0.13 mg/kg; *S*2 had a content range of <0.01–4.50 mg/kg, and an average value of 0.90 mg/kg. For boreholes *Z*1 and *Z*2, the peaks of their *S*2 contents both occurred in the vicinity of horizons with relatively high clay contents, and this was consistent with the lithological trend. Thus, lithology and hydraulic characteristics both influenced the distribution of *S*2. The variation of *S*2 with depth was also consistent with the As content in sediments, suggesting that *S*2 constitutes an important form of As in the sediments.

In *Z*1 and *Z*2 boreholes, the content ranges of the total Fe in the sediments were 12.31–60.01 (28.42 on average) and 15.31–62.73 (32.23 on average) g/kg, respectively (Figs. 3c and g). The total Fe in sediments along depth showed a similar pattern as As, suggesting that there is a relatively high correlation between As and Fe behaviors in the sediments.

3.2.2. Hydraulic characteristics of sediments

The particle size distribution of the sediments determines the physical properties of aquifers, and particle size distribution data can be used to calculate the hydraulic conductivity coefficient (K_f) of an aquifer and evaluate its water permeability.

Fig. 4 shows the variations of the hydraulic conductivity coefficients of the two boreholes by depth. The *Z*1 borehole had a K_f range of 0.010–15.3 m/d, and an average value of 2.98 m/d, and the *Z*2 borehole had a K_f range of 0. 008–14.1 m/d, and an average value of 3.03 m/d. The hydraulic conductivity coefficients of the aquifers in the two boreholes were similar, and they both increased along with increasing depth. This was because the distribution of coarse sand gradually increased in aquifers after exceeding depths of 27 m.

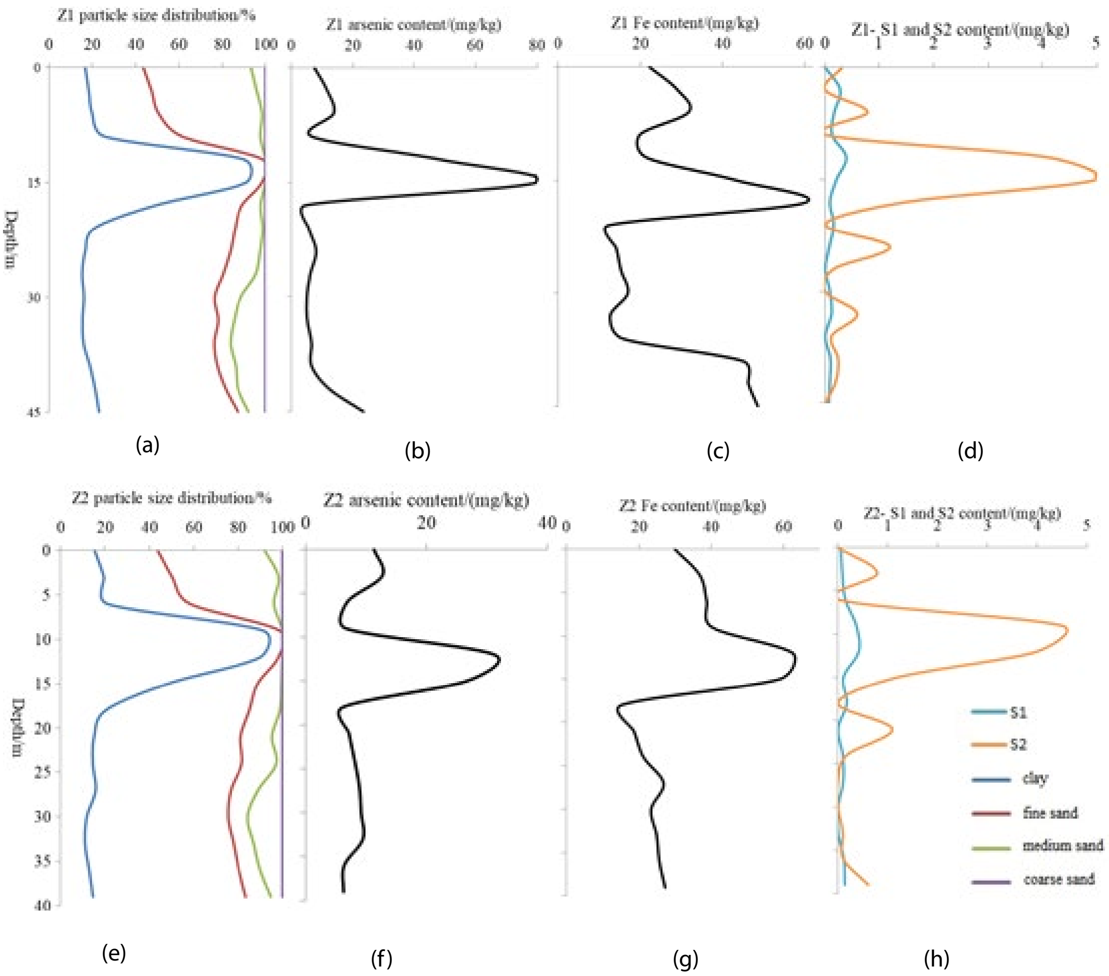


Fig. 3. Vertical profiles of particle size (a and e) and total As (b and f), Fe (c and g), *S*1, *S*2 (d and h) in sediments of *Z*1 and *Z*2 from flood and drip irrigation area, respectively.

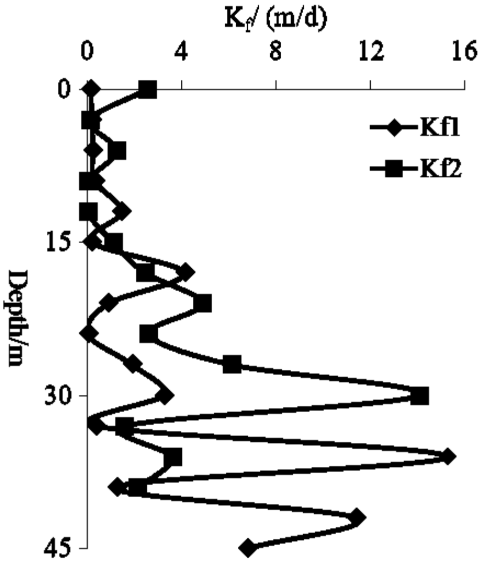


Fig. 4. K_f -values changing with depths of sediments from *Z*1 and *Z*2.

4. Discussion

4.1. Influence of sediment properties on the formation of high-As groundwater

4.1.1. Influence of the particle size distribution in sediments

The particle size distribution in sediments influences the hydraulic connection between groundwater and surface water via K_f, and further affects As behavior. To ascertain the influence of sediments with different particle sizes on the migration and transformation of As, the correlation between the particle percentages of different particle size intervals and As content was analyzed. Depending on size, sediment particles were divided into five classes: $\phi < 16$, $16 < \phi < 20$, $20 < \phi < 63$, $63 < \phi < 200$, and $\phi > 200$ µm. Fig. 5 shows the correlation between the sediment particles of different diameter ranges and the total As, *S*1, and *S*2 in the sediments.

With increasing sediment particle size (from <16 to >200 µm), the correlation with total As, *S*1, and *S*2 varied correspondingly. The content of sediment particles <16 µm in diameter had the highest positive correlation with total As, *S*1, and *S*2, suggesting that sediment particles <16 µm in diameter are most closely correlated with the total As and As

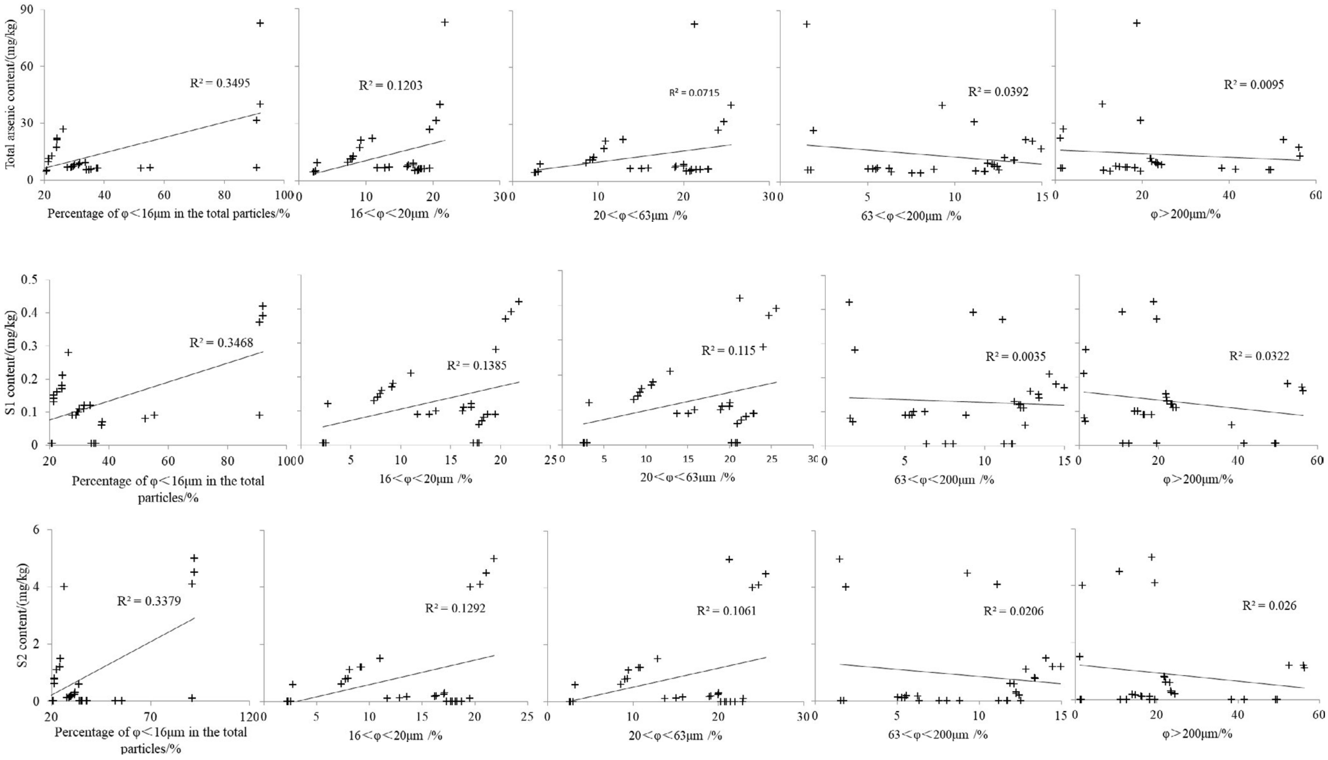
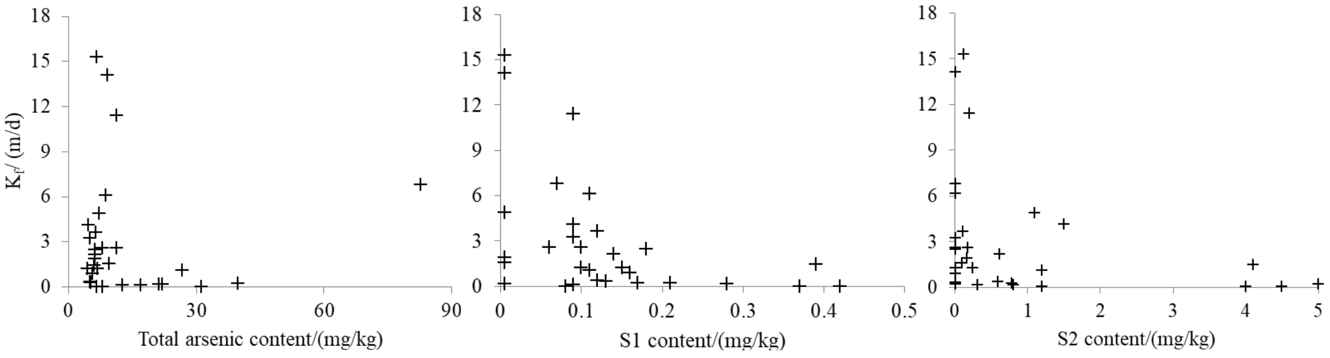


Fig. 5. Relationship between the percentages of different grain sizes and the variations of total As, *S*1, and *S*2 in sediments.



a b c

Fig. 6. Relationship between hydraulic conductivity (K_f) and contents of total As (a), *S*1 (b), and *S*2 (c).

existing state in sediments. This is consistent with the conclusion drawn by Yi et al. [15] in their study on the migration of heavy metals in the sediments collected from the Yangtze Estuary, China. It also suggests that sediment particle size is closely related to As content and existing As state. This is because sediment particles of smaller size have a larger specific surface area and a stronger adsorption capacity, which further facilitates the adsorption of As on the surface of particles. In addition, a higher proportion of small particles in aquifer sediments means poorer hydraulic conditions and a weaker hydraulic connection with the outside world, which further promotes the formation of a local reduction environment and provides conditions for the formation of high-As groundwater [16–18].

There is a negative correlation between the hydraulic conductivity coefficient, K_f, of an aquifer and the total As, *S*1, and *S*2 in sediments (Fig. 6). This correlation suggests that the hydrodynamic conditions of the groundwater have a large influence on the occurrence and migration of As. This is possible because the flow of groundwater transports dissolved organic matter, oxygen, and many other substances, which all have some influence on the migration and occurrence of As between sediments and groundwater [1,19]. An aquifer with a greater K_f has a larger sediment particle size and higher water flow velocity, which has a scouring effect on the As adsorbed on the sediment surface. Under the long-term flow of groundwater, the As adsorbed on sediments is constantly scoured into and migrating with groundwater, therefore decreasing the As content in groundwater. In contrast, an aquifer with a smaller K_f is composed of silty fine sand and fine clay and has a larger specific surface area with charged particle surfaces and stronger adsorption capacity, thus providing absorbing As more readily [20].

Because of the poor hydraulic connection with the outside world, groundwater-surface water does not circulate, resulting in a reducing environment in the aquifer. The organic matters in sediments are preserved, resulting in more microbial activity and a stronger bio-reduction effect, which provides favorable conditions for the presence and release of As [5,21–22]. Thus, in an aquifer with a smaller K_f, there is more total As, *S*1, and *S*2 in the sediments. In addition, Guo et al. [23] also found that the preservation of organic matter in sediments facilitates the enrichment of As.

4.1.2. Influence of Fe/Mn content in sediments on As behavior

The total As, total Fe, and total Mn in the sediments were all positively correlated. As tends to be enriched in sediments with a high content of Fe and Mn (except at individual abnormal sites), suggesting that the adsorption of Fe/Mn oxides provides conditions for the enrichment of As. The presence of local abnormal sites may be related to the difference in the mineral composition of sediments and to other factors. As the sediments bind to Fe/Mn oxides, when the Fe/Mn oxides dissolve, the As adsorbed on Fe/Mn is also released into the groundwater. This process may be the main mechanism that results in high-As groundwater [24]. Thus, in an aquifer with a smaller sediment particle size and a higher clay content, the presence of more Fe/Mn minerals offers sites for the enrichment of As. In contrast, poor hydrodynamic conditions inhibit the connections of groundwater with surface water and atmospheric precipitation, making full oxygen exchange impossible, and easily create a reduction environment that promotes the dissolution of Fe/Mn minerals and release of As.

We found that *S*1 and *S*2 were positively correlated with Fe and Mn levels extracted only within a certain range, and *S*1 and *S*2 had a slightly higher correlation with Mn than with Fe. This may be because: (1) *S*1 was adsorbed mainly via colloid sediments, while *S*2 was mainly bound with the particles with positive charges in sediments, therefore the Fe/Mn content may be influenced to a lesser extent during the extraction process, and (2) the Fe/Mn produced by the dissolution of Fe/Mn oxides was once again adsorbed by Fe-containing oxides (hydroxides). Overall, sediments, especially smaller ones (<16 μm in diameter), can control the flow of groundwater through hydrodynamic conditions and influence the contents of *S*1 and *S*2. Sediments can also affect the enrichment and migration of *S*1 and *S*2 through the amount of Fe and Mn that is adsorbed. In this sense, investigating the properties and distribution of the clay stratum is important for understanding the distribution and formation of high-As groundwater.

4.1.3. Distribution characteristics of As and formation of high-As groundwater

The As in groundwater mainly comes from sediments and is usually controlled by complexation/decomplexation, adsorption/desorption, precipitation/dissolution, redox reactions, and other biological or non-biological reactions [25], all of which are closely related to the circulation of groundwater. According to the results of a hydrochemical analysis on groundwater and a geochemical analysis on sediments, the groundwater in the flood irrigation zone had a relatively low As concentration, but the As content in the sediments in the flood irrigation zone was higher than that in the sediments in the drip irrigation zone. This suggests that the As concentration in groundwater is related not only to the total As in sediments, but also to the mode in which the As occurs. For instance, while it is difficult for As in the crystalline solid phase to migrate into groundwater, As extracted with phosphoric acid can be adsorbed on the surface of sediments through chemical bonds or electrostatic attraction and can thus easily migrate into and transform in groundwater [9]. For this reason, it is necessary to analyze the existing state and distribution characteristics of As in sediments.

As shown in Figs. 3d and h, *S*1 content was lower than *S*2 content. There are several possible explanations for this finding: while there is a relatively significant difference between *S*1 content and *S*2 content in sediments, *S*1 is more susceptible to the scouring effect of groundwater and can engage in ion exchange with Cl^-, PO_4^{3-}, and other ions to migrate into groundwater. According to the study by Van Geen et al. [24] on the Bangladesh region, different existing states of As in sediments have significantly different migration capacities that contribute to the formation of high-As groundwater. To characterize such differences, we introduced the partition coefficient values K_d to evaluate whether different existing states of As contributed to the formation of high-As groundwater. The partition coefficient values K_d of As was used to characterize the migration capacity and separation efficiency of As in solid and liquid phases. K_d is an important physicochemical characteristic parameter used to describe the behaviors of As in the two phases and is defined as the ratio of the As content in sediments to the As concentration in groundwater (unit: L/g). Using this analysis, we found that *S*1 ($R^2 = 0.73$, $n = 8$) and *S*2 ($R^2 = 0.94$, $n = 8$) in the sediments had a positive correlation with As concentration in groundwater (Fig. 7).

The overall macroscopic distribution coefficient K^*_{d-S1} and the overall macroscopic distribution coefficient K^*_{d-S2} were 0.004 and 0.008 L/g, respectively. This result was slightly higher than previous results from Van Geen et al. [24] in Bangladesh (0.004 L/g) and Ni et al. [25] in the Hetao Basin, but slightly lower than levels obtained using H_3PO_4 (0.010 L/g) [7]. Meanwhile, *S*1 could more easily migrate into groundwater than *S*2. *S*1 had a low binding force with sediments and could easily enter groundwater via water flow scouring and ion exchange, thus making a major contribution to the formation of high-As groundwater.

4.2. Influence of land use patterns on the As content of groundwater

As seen in Fig. 1, the drip irrigation zone and the flood irrigation zone both fell within the scope of the downstream

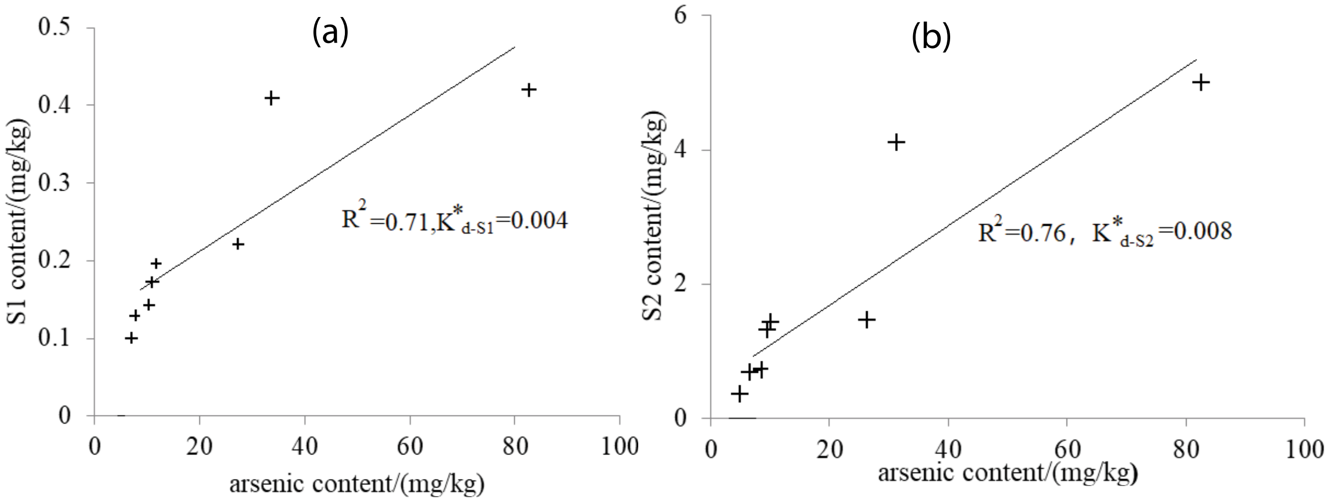


Fig. 7. Relationship between contents of *S*1 (a), *S*2 (b) and dissolved arsenic concentration at matched depths.

fine soil plain of the Kuitun River Basin. The drip irrigation zone and the flood irrigation zone had similar sediment compositions, but the As concentration in groundwater in the drip irrigation zone was higher, possibly caused by the different land use patterns in the two zones (Figs. 3a and e). The flood irrigation zone is dominated by vegetable agriculture, which creates high water demand. When soil is below the irrigation water level on a long-term basis, it modifies groundwater's connection with the outside world and its natural replenishment relationship with aquifers or even changes the aquifer properties and boundary conditions. The primary source of irrigation water in the flood irrigation zone is from the Kuitun River, which comprehensively influences the As concentration in groundwater via dilution and the redox environment.

Due to its relatively low As and ion concentrations, the river water diluted the groundwater when there was a hydraulic connection between them. What's more, the Kuitun river water contains a great quantity of dissolved oxygen and organic matter, and long-term vertical infiltration connects irrigation water and groundwater. As a result, the irrigation water carrying abundant dissolved oxygen and organic matter infiltrates into aquifers, and the oxidization process of organic matter modifies the redox environment to some extent, placing them in a reduction state, increasing microbial activity [26], and facilitating the release of As from sediments to groundwater. Seen from the influence of the water of the Kuitun River in the above two aspects and the monitoring results of the As concentration in groundwater, the dilution process of the water of the Kuitun River in the flood irrigation zone may have played a dominant role.

In contrast, the drip irrigation zone is dominated by cotton plantations. Its main irrigation regime is intermittent irrigation, which requires less water and creates a weaker dilution effect in comparison to the flood irrigation zone. As a result, the As concentration in groundwater in the drip irrigation zone is slightly higher than groundwater in the flood irrigation zone. The water source of the drip irrigation zone is groundwater, which has a limited influence on its reduction environment and promotes the release and migration of As. In addition, cotton requires higher levels of phosphorus fertilizers than vegetables, but they have similar utilization rates of phosphorus fertilizers [27]. For this reason, compared to the flood irrigation zone, the drip irrigation zone has more residual phosphates in soil. With leaching by irrigation water, phosphates enter groundwater and further increase the concentration of PO_4^{3-}. From the test results of groundwater, it can be observed that the groundwater in the flood irrigation zone dominated by vegetable agriculture had a PO_4^{3-} concentration of 234 μg/L, while that in the drip irrigation zone dominated by cotton agriculture had a PO_4^{3-} concentration of 324 μg/L. The competitive adsorption by phosphates caused the As originally adsorbed on the surface of minerals to be released into groundwater.

Thus, in some high-As regions, the harm of high-As groundwater can be alleviated through changing land-use patterns and introducing low-As irrigation water. This also suggests that the concentration of competitive ions in groundwater constitutes a key factor influencing the formation of high-As groundwater.

5. Conclusions

- From the alluvial–proluvial plain to the fine soil plan downstream of the Kuitun River Basin, the hydrochemical type of the groundwater experienced a transition from $HCO_3{\cdot}SO_4$–$Ca{\cdot}Mg$ to $Cl{\cdot}SO_4$–$Na{\cdot}Ca$, and high-As groundwater was mainly distributed at depths of 20–36 m. The alluvial–proluvial plain had the lowest As concentration in groundwater, followed by the flood irrigation zone and finally the drip irrigation zone, and average As concentrations were 9.6, 36.0, and 151.5 μg/L, respectively.
- The sediments collected from the flood irrigation zone and the drip irrigation zone mostly led to interbedding of sand-(silty) fine sand-clay. The average total As, *S*1, and *S*2 contents of the flood irrigation zone were 15.8, 0.12, and 0.89 mg/kg, respectively, while those of the drip irrigation zone were 11.2, 0.13, and 0.90 mg/kg, respectively. A horizon with a higher clay content usually had a higher As content. Particle size grading analysis found that the average clay, fine sand, and medium sand contents in

the sediments collected from the flood irrigation zone were 29.8%, 76.1%, and 93.7%, respectively, and clay was mainly distributed in the horizons from 0–3 and 12–15 m. The average clay, fine sand and medium sand contents in the sediments collected from the dry farmland zone were 28.9%, 77.2%, and 94.5%, respectively, and clay was mainly distributed from the 9–12 m horizon. There was no significant difference between their average hydraulic conductivity coefficients of 2.98 and 3.03 m/d.

- Sediment particles of different sizes influence the As behavior in sediments to varying degrees. The content of sediment particles <16 μm in diameter were positively correlated with total As, *S*1, and *S*2 content, and had the strongest influence on As behavior in sediments. There was a negative correlation between K_f and the total As, *S*1, and *S*2 in sediments. Fe/Mn oxides were positively correlated with As, and their reductive dissolution constitutes one of the important processes related to the formation of high-As groundwater. As indicated by the analysis on the correlation of the As partition coefficient values K_d with *S*1, *S*2, and PO_4^{3-}, the migration and transformation of As between sediments and groundwater was influenced by the mode in which As occurred, competitive ions, and other factors. The competitive adsorption by ions, such as PO_4^{3-}, appears to be an important way in which As is released into groundwater.
- Human activities, especially land-use patterns, influence As behavior. Specifically, the differences in irrigation regimes and fertilization patterns can largely explain the different As concentrations in groundwater in the drip irrigation zone and the flood irrigation zone. The differences in irrigation regimes were caused by water source and water quantity. Due to continuous irrigation using water from the Kuitun River in the flood irrigation zone, the degree of dilution of groundwater in the flood irrigation zone was higher than that of groundwater in the drip irrigation zone. In addition, the groundwater in the drip irrigation zone had a relatively high PO_4^{3-} concentration. This was caused by the higher usage of phosphorus fertilizers in the cotton growers in the drip irrigation zone, leading to higher residual phosphates in the soil. With leaching by irrigation water, phosphates entered groundwater, further increasing the concentration of PO_4^{3-} in groundwater. The competitive adsorption by PO_4^{3-} caused the As originally adsorbed on the surface of minerals to be released into groundwater. The above two aspects can largely explain the higher As concentration in the drip irrigation zone was higher compared to the flood irrigation zone.

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