

Article Hydrogeochemical Processes and Potential Exposure Risk of Arsenic-Rich Groundwater from Huaihe River Plain, China

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Abstract: Arsenic poses a danger to environmental health, and arsenic-rich groundwater is a key exposure risk for humans. The distribution, migration, and enrichment of arsenic in groundwater is an important environmental and public health problem. Currently, the Huaihe River Basin is identified as a region of arsenic-rich groundwater in China. This study aims to assess arsenic-rich groundwater potential pollution risk, analyze the hydrogeochemical processes, and trace the ion source based on an analysis of groundwater hydrogeochemical data. The results show that arsenic is the main inorganic chemical substances affecting the water quality in the study area, which presents a high exposure risk for public health. The arsenic concentration of groundwater was f $5.75 \pm 5.42 \,\mu$ g/L, and 23% of the considered samples exceeded the drinking water standards of the World Health Organization. The groundwater in the study area underwent evaporation, halite dissolution, and ion exchange processes. The total alkalinity (HCO₃⁻) of the arsenic-rich groundwater mainly ranged between 400–700 mg/L, and the chemical type was mainly of HCO₃-Na. In an alkaline environment, the oxidative dissolution and reductive dissolution of arsenic bearing minerals might be the formation mechanism of arsenic-rich groundwater.

Keywords: arsenic; hydrogeochemistry; pollution risk; arsenic source; water-rock interaction

1. Introduction

Arsenic (As) is ubiquitous in nature and listed as a Class I specific carcinogen by the International Agency for Research on Cancer (IARC) [1–3]. The most sensitive toxicity threshold of As concentration in drinking water has not been determined. The recommended limit of As concentration in drinking water is $10 \ \mu g/L$, according to the guidelines for drinking-water quality by the World Health Organization (WHO) [3]. According to the United States Environmental Protection Agency (EPA) and the National Research Council (NRC), the long-term consumption of water with As concentrations as low as $5 \ \mu g/L$, or even $3 \ \mu g/L$, might cause adverse chronic health effects on humans, especially cancer [4,5]. Drinking arsenic-rich groundwater is the main route for human exposure to this element.

High arsenic groundwater is widely distributed in South Asia, Southeast Asia, West Africa, North America [2,6–13]. Globally, more than 100 million people are exposed to arsenic-rich groundwater, including 19 million in China [2,14–16]. The formation of arsenic-rich groundwater is a result of the combined action of multiple factors and complex geological processes. Many researchers conducted in-depth and extensive geochemical studies on the distribution of arsenic-rich groundwater. They analyzed its formation and evolution and traced the source of arsenic and its dissolution and release mechanisms [17–28]. Arsenic enrichment in groundwater was probably released from arsenic-bearing aquifers through oxidative and (or) reductive dissolution [2,6,9,13,28,29].

The high mortality and incidence rates of cancer in the Huaihe River Basin have been widely reported since the 1980s. The high probability of arsenic hazards in this region



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). might suggest the hypothesis that groundwater arsenic contamination via consumption contributed to this cancer cluster. Therefore, the enrichment of arsenic in groundwater in this area received extensive attention, and preliminary hydrogeological environmental surveys and scientific research were conducted [16,30–32]. A statistical prediction based on the groundwater data from the Huaihe River Basin was conducted in 2010, which provided evidence that arsenic exposure via groundwater was possibly associated with the severe cancer phenomenon. The survey found that the proportion of arsenic concentration exceeding 10 μ g/L in the monitored wells was 17%, with the highest detection value being 620 μ g/L [16]. Previous research mainly focused on the hydrogeochemical distribution of arsenic-rich groundwater and the geographical distribution of endemic diseases as a consequence of water arsenic poisoning through drinking water. Such research lacked thorough analyses of the formation processes, evolution mechanisms, and influencing factors that result in arsenic-rich groundwater.

Given the extensive harmful effects of arsenic on the natural environment and public health, conducting geochemical studies on arsenic pollution in the groundwater of the Huaihe River Basin is necessary. This study selects the representative localized flow field of arsenic-rich groundwater in the Huaihe River Plain (Taihe County, Anhui Province) to analyze the hydrogeochemical characteristics and identify the formation processes. Based on the hydrogeochemical data analysis, the objective of this study is to (1) analyze the hydrogeochemical characteristics and evaluate their pollution risk; (2) identify the hydrogeochemical processes; and (3) trace the source of arsenic and its mobilization process.

2. Materials and Methods

2.1. Outline of the Study Area

The Huaihe River Basin is located in Eastern China. It originated in the Tongbai and Funiu Mountains in the west, which face the Yellow Sea in the east. It extended between a $30^{\circ}55' \sim 36^{\circ}36'$ N latitude and $111^{\circ}55' \sim 121^{\circ}25'$ E longitude with a total area of 2.7×10^4 km². The climate in this region is generally described as a warm temperate sub-humid monsoon climate. The monthly mean temperature ranges from 0 °C in January to 25 °C in July, with a mean annual temperature of $11\sim16$ °C, respectively. Rainfall is also highly seasonal, with a mean annual total of 920 mm, $60\%\sim80\%$ fall in spring and summer. The Huaihe River Basin is geologically located at the junction of three tectonic units that are the North China Block, Yangtze Block, and Qinling Orogenic Belt [16,33,34]. The terrain tilts slightly from the northwest to southeast, with the alluvial–proluvial plain as the main landform. The terrain is flat, with the sea-level elevation generally ranging from 15 to 50 m (Figure 1).

The study area was covered by unconsolidated sediments from the Early Pleistocene to the Holocene. The basement under the loose sediments was composed of Neogene strata. The Cenozoic deposit was approximately 500-600 m thick and was composed of materials derived from acidic silicate rocks. Quartz and feldspar were the dominant minerals. The plain is characterized by several porous aquifer systems (Figure 1). The permeable layers consisted of unconsolidated sands, which were separated by layers of poorly permeable silt clays. The stratigraphic sequence was divided into shallow and deep aquifer systems, and groundwater flow ran from northwest to southeast generally. The uppermost unit in the study area was a shallow porous water system, which contained a series of Holocene and Late Pleistocene sediments. These sediments included fine sands and loamy clay that were laterally discontinuous, resulting in a highly heterogeneous aquifer system. The unconfined aquifer was generally less than 40 m deep, and the water table was at a depth of 2-6 m. The phreatic aquifer was recharged by local rainfall and surface water and discharge through evaporation generally. There was a deep porous water system underneath the phreatic aquifer, which formed during the Middle, Early Pleistocene to Neogene. The deep system was composed of fine sands, silts and gravels. The deep aquifer was generally at a depth of 50 to 500 m, and the water table was 10–50 m deep. The deep aquifers that were separated by cohesive soil layers could not directly receive the recharge from



the atmospheric precipitation. The deep groundwater flow was slow and showed weak regeneration, and pumping was the main way to discharge the deep groundwater.

Figure 1. Sampling points and hydrogeological profile from Taihe, Anhui Province in the Huaihe River Basin, China.

2.2. Sampling and Methods

In this study, we selected a small-scale zone of arsenic-rich groundwater in Maji Town as a natural experimental field to collect groundwater and sediment samples (Figure 1). Figure 1 shows the results of sampling and analysis in May and September 2019. The groundwater sampling points were selected via the grid method, with sampling intervals from 2 km \times 2 km to 4 km \times 4 km, and 62 water samples were collected. The water samples were collected from boreholes using standard sampling procedures [35]. All the groundwater samples were from the shallow aquifer. The aquifers consisted of quaternary

sandstone, fine sandstone, and siltstone. An instantaneous sampling method was implemented for the groundwater sample collection. All the water samples were collected and stored in polyethylene plastic bottles. The samples for major ion analysis were filtered. Before sampling, the sample bottles and stopcocks were washed three to five times with the water to be collected; then, the samples were acidified with nitric acid (pH < 2) for the analysis of cations. The pH, temperature, redox potential, and total dissolved solids (TDSs) were measured in the field using portable meters (HANNA, HI8424; THERMO scientific, ORION) and calibrated using standard solution. All the samples were kept in a refrigerator (temperature ~4 °C) during transport to the laboratory and analyzed within 48 h. In addition, 42 sediment profiles were positioned in the experimental field, which were evenly distributed over the entire region. The sediment samples were taken from 50~100 cm depths in the profiles. The samples were prepared for testing after the process of drying and cleaning, and then ground to 0.15 mm sized particles.

The hydrochemical concentrations of ions, such as As; K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, SO_4^{2-} , HCO_3^- , F^- and Br^- , the total alkalinity, and total acidity were determined at the Laboratory of the China Geological Survey, Nanjing Center. The arsenic concentration in the groundwater was determined by atomic fluorescence spectrometry. The detection limit of arsenic by a fluorescence spectrometer (AFS-820, Bojin, Zhengzhou, China) was 0.05 µg/L, with <1.0% precision. Cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) were determined by inductively coupled plasma-atomic emission spectrometry (ICP-OES), while anions (SO₄²⁻, Cl⁻, F⁻, Br⁻) were determined via ion chromatography. Total alkalinity and total acidity, and HCO₃⁻ were determined by acid titration. The sediment samples collected for X-ray diffraction were determined by an X-ray diffractometer (D/MAX 2500, Tokyo, Japan) at the Laboratory of the China Geological Survey, Nanjing Center.

All constituents were analyzed in duplicate and the mean values were used in calculations. Deionized water was used to assure the quality control of the analyses and revealed a relative standard deviation (<5%).

The WHO guidelines for drinking water were applicable to countries around the world, but China's standards for drinking water were not known by foreign scientists. Therefore, the WHO guidelines were cited for evaluating the drinking water quality in this study.

Gibbs (1970) [36] plots, which are plots of TDS against Na⁺/(Na⁺ + Ca²⁺) and Cl⁻/(Cl⁻ + HCO₃⁻), are a convenient graphical method for identifying the natural processes (water–rock interaction, precipitation, and evaporation) that control the evolution of the major ion chemistry of groundwater. The Gibbs diagram was originally developed for surface waters, therefore the use of the Gibbs diagram for defining groundwater geochemical processes might oversimplify the interpretation of aquifer systems and overlook important processes [37]. However, Gibbs plots have been widely used for identification of hydrogeochemical processes [5,25,38,39].

According to the principle of thermodynamics, the dissolution and precipitation of minerals in water–rock reactions are determined by the saturation index (SI) of various minerals in groundwater [40,41]. The mathematical expression of SI is

SI = lg IAP/Ks

where IAP is the solubility product and Ks is the equilibrium constant of the mineral.

For the statistical analysis, SPSS19.0 was used as a platform for the descriptive statistical analysis, correlation analysis, and regression analysis. Phreeqc 3.40 was selected for the determination the mineral phase and saturation indices [40]. The thematic maps were produced by using Coreldraw X4 and AquaChem 3.70.

3. Results and Discussion

3.1. Hydrochemistry and Pollution Risk

According to the results of the hydrochemical analysis (Table S1), the TDS concentration of the shallow groundwater is $719 \pm 310 \text{ mg/L}$. Most of the samples were low-salinity fresh water (<1000 mg/L) and 26% was in the range of brackish water (1000–3000 mg/L)

according to China's hydrological guideline [35]. The mean annual temperature of the groundwater samples was approximately 15.5 °C, with a range of 14.6 °C–17.3 °C. The average pH value was 7.31, with a range of 7.01–8.19, which showed little variation across the study area. The measurement of the in situ redox potential ranged from -20.5-342 mV, with a mean redox potential of 214 mV, and most of the groundwater samples were oxidizing rather than reducing. HCO_3^- was the dominant anion in the groundwater samples, followed by SO_4^{2-} and Cl^- , with concentrations of 617 ± 220 , 83.7 ± 73.1 , and 54.0 ± 58.8 mg/L, respectively. Na⁺ was the dominant cation, followed by Ca²⁺ and Mg²⁺, with concentrations of 186 \pm 120, 46.2 \pm 27.9 and 39.5 \pm 12.4 mg/L, respectively. According to the drinking water quality standards recommended by the WHO (2011), the main factors affecting the groundwater quality in the study area were the concentrations of arsenic and fluoride. The arsenic concentration of groundwater in the study area was $5.75 \pm 5.42 \,\mu g/L$, showing clear spatial variability. The proportion of arsenic-rich groundwater samples above >1 μ g/L reach 74%, and the ratio of test samples that exceeded 10 μ g/L is 23% (Figure 1). The fluoride concentration of groundwater was 1.29 ± 0.40 mg/L, and 31% of the considered samples exceeded the WHO-recommended limit of 1.50 mg/L.

The dominant ions determine the groundwater types. According to the Piper diagram (CGS, 2012), the groundwater types in the study area are dominated by HCO₃—Na, followed by HCO₃—Na•Mg, HCO₃—Na•Ca, and HCO₃—Na•Ca•Mg. The arsenic-rich groundwater types are dominated by HCO₃—Na (Figure 2).



Figure 2. Piper diagram of the groundwater samples from Taihe, Anhui Province in the Huaihe River Basin, China.

Alkalinity in the natural water mainly depended on the presence of bicarbonate (HCO₃⁻), carbonate (CO₃⁻), and hydroxide (OH⁻). The total alkalinity of the test samples was $515 \pm 169 \text{ mg/L}$, the total acidity was $20.0 \pm 4.63 \text{ mg/L}$, and the groundwater was alkaline. According to the law of carbonate balance, when the pH value is 4.5–10, the HCO₃⁻ alkalinity occurs. When the pH value is ≤ 8.32 , all CO₃²⁻ is converted to HCO₃⁻ [39,42,43]. The total alkalinity of the test samples had a highly significant positive correlation with the

concentration of HCO₃⁻, with a correlation coefficient R = 0.997 ($p \le 0.01$). Therefore, the total alkalinity in the water samples was HCO₃⁻ alkalinity and it generally reflected the content of HCO₃⁻. The total alkalinity of arsenic-rich groundwater mainly ranges between 400–700 mg/L (Figure 3). The weathering of carbonate mineral and ion exchange reactions in the study area influenced the alkalinity of the groundwater.



Figure 3. Diagram of total alkalinity in the groundwater from Taihe, Anhui Province in the Huaihe River Basin.

3.2. Hydrogeochemical Processes

3.2.1. Evaporation and Dissolution Processes

According to the Gibbs diagram (Figure 4), TDS in the study area is $722 \pm 296 \text{ mg/L}$, Cl/(Cl + HCO₃) ranges from 0.01 to 0.03, and Na/(Na + Ca) ranges from 0.23 to 0.94. Most of the analytical samples are located in the areas of water–rock interaction and evaporation crystallization (Figure 4), confirming that the water–rock interaction and evaporation processes have an impact on the formation and evolution of groundwater in the study area.



Figure 4. Gibbs diagram of hydroeochemistry from Taihe, Anhui Province in the Huaihe River Basin, China.

3.2.2. Evaporation and Concentration Processes

The solutes also commonly found in the groundwater were Cl and Br. Due to the conservative behavior and high solubility of Cl and Br in natural water, ion exchange reaction and mineral surface adsorption could not significantly change the concentrations of Cl and Br. With the increase in chloride ion concentration, the dissolution of halite (NaCl) would produce a rapid increase in the Cl/Br ratio. In contrast, the evaporation process of groundwater could change the absolute concentrations of Cl and Br in the groundwater, but would not change the Cl/Br ratio before the groundwater was saturated with halite. Therefore, the Cl, Br, and Cl/Br ratio could be used to identify and distinguish the dissolution, evaporation, and other evolution processes of groundwater [5,40,44–47]. The Cl^- concentration range of the test samples was 0.70–210 mg/L, the mean value was 54.0 ± 58.8 mg/L, the Br⁻ concentration range was 10.7–324 µg/L, and the mean value was $104 \pm 88 \,\mu g/L$. There was a moderately significant positive correlation between the Cl⁻ and Br⁻ concentrations, with a correlation coefficient of 0.75 ($p \le 0.01$). Cl⁻ and Br⁻ concentrations of the test samples were relatively low, the mean value of Cl/Br (mol) was 1097 ± 1044 , and the ratio varied from 51.0 to 4603. A majority of Cl/Br ratio of the test samples exceeded 600, showing significant spatial variability (coefficient of variation = 0.95). The Cl/Br ratio of water samples above the WHO limit (>10 μ g/L) ranged from 544 to 3093, with an average of 993. The mineral structure of halite (NaCl) did not contain a large number of Br, and its Cl/Br ratio were generally 10⁴–10⁵. The dissolution of halite would result in a rapid increase in the Cl/Br ratio with the increase in Cl⁻ concentration. The highest value of Cl/Br ratio of the test samples exceeded 4600, and the concentration of Cl⁻ in groundwater did not exceed 6 mmol/L. The dissolution of a small amount of halite in groundwater was the most likely mechanism for the rapid increase in the Cl/Br ratio. The large variation range of Cl/Br ratio reflected the different dissolved amount of halite in each test sample. As shown by the relationship between the Cl/Br ratio and Cl concentrations (Figure 5), evaporation and halite dissolution are the dominant processes controlling groundwater formation and evolution. The Cl/Br ratio of arsenic-rich groundwater were relatively unchanged with the increase in Cl⁻ concentrations, indicating that the arsenic-rich groundwater was more affected by evaporation.



Figure 5. Correlation diagram of the Cl/Br ratio and Cl in the groundwater from Taihe, Anhui Province in the Huaihe River Basin, China.

3.2.3. Weathering Hydrolysis Processes

The Ca/Na, Mg/Na, and HCO₃/Na(mol) ratios could be used to obtain relevant information on the groundwater source and water quality evolution [38,39]. As shown by the diagram of Mg/Na-Ca/Na and HCO₃/Na-Ca/Na in the study area (Figure 6), the Mg/Na and HCO₃/Na ratio of groundwater gradually increases with the increase in the Ca/Na ratio. The cation concentration ratio of groundwater was mainly distributed between the dissolution of evaporative minerals and silicate minerals, and partly distributed between the dissolution of carbonate minerals and silicate minerals, indicating that the groundwater in the study area was under the effects of evaporative dissolution, silicate weathering, and carbonate dissolution. The arsenic-rich groundwater was mainly distributed between the dissolution of evaporative minerals and silicate minerals, and was affected by evaporative dissolution and silicate mineral weathering to a greater extent. This implied that evaporative dissolution and silicate mineral weathering effects influenced the arsenic-rich groundwater more significantly.



Figure 6. Diagram of Ca/Na-Mg/Na and HCO₃/Na-Ca/Na in the groundwater from Taihe, Anhui Province in the Huaihe River Basin.

3.2.4. Ion Exchange Processes

The Na/Cl ratio (mol) is a hydrogeochemical parameter characterizing the degree of Na⁺ enrichment in groundwater that could be used to reflect the degree of ion exchange [5,43,45,47]. The Huaihe River Basin is an arid/semi-arid region with strong evaporation, which leads to the accumulation of halite in the sedimentary layer. The dissolution of halite is one of the sources of Na⁺ and Cl⁻ in the groundwater in basins. If the dissolution of halite was the main source of Na⁺ and Cl⁻, the ratio of Na/Cl (mol) should be 1:1, and Na⁺ above this ratio probably underwent ion exchange processes. In this study, the Na/Cl ratios of the groundwater samples collected in the entire region were 9.63 \pm 57.4, and those for most of the samples were substantially larger than 1:1, showing significant spatial variability. The Na/Cl ratio decreased with the increase in Cl concentration. The Na/Cl ratios of the contaminated groundwater (As \geq 10 µg/L) were 15.7 \pm 16.0, above the dissolution line of halite. Therefore, this infers that the Na⁺ in groundwater in the study area not only derives from a halite dissolution, but also originates from ion exchange processes. Moreover, ion exchange is more significant with an As content increase (Figure 7).



Figure 7. Diagram of Na-Cl in the groundwater from Taihe, Anhui Province in the Huaihe River Basin, China.

3.3. Ion Source and Arsenic Mobilization

The saturation index (SI) was used to identify the water quality and hydrochemical evolution process [5,39,45]. SI < 0, SI = 0 and SI > 0 were the thermodynamic criteria for the dissolution, equilibrium, and precipitation of minerals, respectively, and 0.5 >SI > -0.5 was generally considered as near saturation. In this study, the SI of the water samples was calculated using PHREEQC at 15.5 °C, ph = 7.31 (Table S1). The calculation elements of input were the measurements of K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, HCO₃⁻, F⁻, and Br⁻. The SI values of the minerals, calcite (-0.01 ± 0.16), aragonite (-0.16 ± 0.16), and dolomite (0.17 ± 0.29), were close to 0, which meant that the groundwater was near-saturated with respect to these minerals. The SI values of the unsaturated minerals, halite (-7.09 ± 0.87), gypsum (-2.19 ± 0.47), anhydrite (-2.70 ± 0.90), sylvite (-8.94 ± 0.73), and fluorite (-1.06 ± 0.21), are less than -0.5, indicating a dissolution tendency (Table 1). Cl⁻, F⁻ and SO₄²⁻ in groundwater were partly derived from the dissolution and release of halite, fluorite, gypsum, sylvite, and anhydrite minerals.

Table 1. Saturation indices of the groundwater from Taihe, Anhui Province, in the Huaihe River Basin, China.

Sample Grouping ID	SI(h)	SI(g)	SI(an)	SI(d)	SI(c)	SI(ar)	SI(f)	SI(sy)
$As < 3 \ \mu g \ L^{-1}$	-7.33 ± 0.86	-2.15 ± 0.43	-2.57 ± 0.43	-0.19 ± 0.31	-0.03 ± 0.20	-0.12 ± 0.20	-0.97 ± 0.20	-9.06 ± 0.66
$5 > As \geq 3 \ \mu g \ L^{-1}$	-7.54 ± 0.59	-2.13 ± 0.34	-2.55 ± 0.33	0.29 ± 0.16	0.01 ± 0.11	-0.14 ± 0.11	-1.10 ± 0.25	-8.67 ± 0.70
10 > As $\geq 5~\mu g~L^{-1}$	-7.03 ± 1.03	-2.31 ± 0.64	-2.74 ± 0.61	0.05 ± 0.35	-0.07 ± 0.15	0.22 ± 0.15	-1.13 ± 0.17	-8.99 ± 0.92
$As \geq 10 \ \mu g \ L^{-1}$	-6.90 ± 0.81	-2.15 ± 0.43	-3.00 ± 1.70	0.18 ± 0.22	-0.01 ± 0.12	-0.16 ± 0.12	-1.12 ± 0.17	-8.85 ± 0.67

SI(h): halite, SI(g): gypsum, SI(d): dolomite, SI(c): calcite, SI(f): Fluorite, SI(an): anhydrite, SI(ar): aragonite, and SI(sy): SI(Sylvite).

Under the pH and Eh conditions of the natural environment, As existed mainly as As (V) in an oxidative state or As (III) in a reductive state. Arsenic minerals in sediments usually existed in mineral phases, such as arsenate, arsenite, and sulfide. There were many possible hydrogeochemical factors that triggered the release of arsenic from the solid phase into the groundwater. The oxidative dissolution and reductive dissolution of arsenic-bearing minerals were the main processes of geogenic arsenic being released from the sediments to the groundwater. Changes in the groundwater regime, redox potential (Eh), acidity, and alkalinity (pH) exerted an influence on arsenic in the sediments, through

the adsorption and resolution process, and then affected the concentration of arsenic in the water [5,11,15,19,27,29,41,48–52].

The SO₄²⁻ in the groundwater could be derived from both gypsum dissolution and sulfide oxidation. There is a positive correlation between the As and SO₄²⁻ contents in the test samples (correlation coefficient R = 0.58) (Figure 8). The mean concentrations of SO₄²⁻ in the groundwater with As < 3, $3 \le \text{As} < 5$, $5 \le \text{As} < 10$ and $\text{As} \ge 10 \,\mu\text{g/L}$ in the analytical samples were 0.74, 1.09, 0.92, and 0.93 mmol/L, respectively. The SO₄²⁻/Ca²⁺ (mol) ratio of the groundwater in the entire region was 0.76. SO₄²⁻ in the groundwater originated not only from the dissolution of gypsum minerals, but also from the oxidation of sulfide.



Figure 8. Correlation analysis of $As-SO_4^{2-}$ in the groundwater from Taihe, Anhui Province in the Huaihe River Basin.

According to the phase analysis attained form the X-ray diffraction, the main mineral components of the sediments in the Huaihe River Basin were quartz, potash feldspar, calcite, and clay minerals, in the contents of 47.1%, 3.79%, 8.27%, and 33.4%, respectively. There was a small amount of pyrite and siderite in some samples, and the counterpart contents were 2.5% and 47.1%, respectively, but no hematite was detected. The presence of reducing minerals showed a reductive hydrogeological background. Arsenic sulfide was a stable host of arsenic, and its associated arsenic was highly correlated with the occurrence of groundwater arsenic. Therefore, it was speculated that arsenic in the sediment from the Huaihe River Basin might exist as arsenic-bearing sulfide phase under reductive conditions, and the dissolution of arsenic-bearing minerals was a source of arsenic.

Due to the long-term exploitation of groundwater in large quantities, the environment of the groundwater flow system changed, breaking the equilibrium of the dynamic exchange between the solid and liquid phases of the aquifers, and triggering the release of arsenic from the solid phase into the groundwater. The dissolution of carbonate minerals usually increased the alkalinity (pH). Under high pH conditions, the oxidation of arsenic-containing sulfide led to the release of arsenic, iron, and sulfur into the groundwater, promoting the concentration of As and SO_4^{2-} . In addition, desorption and ion exchange under alkaline pH conditions could enhance arsenic enrichment in the groundwater. Therefore, it was speculated that the oxidative dissolution and reductive dissolution of arsenic-bearing minerals in aquifers were the main processes leading to the release of geogenic arsenic into the groundwater. Evaporite minerals (halite, fluorite, gypsum, and anhydrite) were probably the source of elevated levels of Cl, F, and SO_4^{2-} .

4. Conclusions

The formation of arsenic-rich groundwater required the combined action of multiple factors in the process of water–rock interaction, such as the accumulation of arsenic-bearing

minerals, the dissolution and precipitation of solid arsenic, and the hydrogeological conditions of arsenic enrichment. The Huaihe River Basin is a typical area of arsenic-rich groundwater in China. In this study, we selected a typical small-scale region of arsenic-rich groundwater in the basin for the natural field experiment to analyze the formation and evolution of arsenic-rich groundwater and trace the source of arsenic and its release mechanism. The concentration of arsenic in the study area was $5.75 \pm 5.42 \,\mu$ g/L, showing clear spatial variability. The proportion of groundwater with a high As content (>10 μ g/L) reached 23%, showing a high exposure risk. According to the analysis of the hydrochemical composition, the groundwater in the study area underwent the processes of evaporation, halite dissolution, and water–rock interaction. Cl⁻, F⁻, and SO₄²⁻ in the groundwater were partly derived from the dissolution and release of halite, fluorite, gypsum, and anhydrite minerals. The chemical type of arsenic-rich groundwater was mainly HCO₃-Na. The arsenic-rich groundwater was of an in situ origin, and it was likely that the arsenic derived from the dissolution and release from aquifer sediments.

Based on the analysis of the hydrogeochemical data, this study speculated the arsenic source and its mobilization process, even though it lacked any concrete evidence to support the hypothesis. The speciation and composition of arsenic in sediments influenced the concentration, activity, and toxicity of arsenic in groundwater. In order to understand the formation mechanism of arsenic-rich groundwater, future studies should focus on the distribution and speciation of geogenic arsenic in aquifers.

Supplementary Materials: The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/w14050693/s1, Table S1: Groundwater quality data and saturation indices (SI) from the Taihe, Anhui Province in Huaihe River Basin (sampled in June and September 2019).

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Conflicts of Interest: The authors declare no conflict of interest.

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