

## Article

# Spatial Distribution of Arsenic in the Aksu River Basin, Xinjiang, China: The Cumulative Frequency Curve and Geostatistical Analysis

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**Abstract:** The quality of drinking water is crucial for human health and the sustainable development of societies. The Aksu River Basin, a typical inland river system, has areas where groundwater arsenic levels exceed safe drinking water standards (i.e., arsenic concentrations greater than 10 µg/L). Identifying the causes of high arsenic levels in the basin's groundwater requires further study. Analyzing the hydrogeochemical composition of the Aksu River basin helps us to understand the spatial distribution of groundwater environments and locate areas with dangerously high arsenic levels. In this research, we collected 196 groundwater samples from along the river. Out of these, 38 samples had arsenic levels above 10 µg/L, which represents 19.4% of the total samples collected. By examining the slope changes in the cumulative frequency curves of major ion ratios and employing geostatistics (specifically, the Kriging interpolation), and taking into account the environmental characteristics of the entire basin, we divided the study area into five sub-regions (Zone I through Zone V). The geostatistical analysis showed a significant spatial variability in groundwater arsenic levels, with a clear spatial correlation. Our findings demonstrate that arsenic concentrations in the Aksu River basin's groundwater vary widely, with Zones II and III—mainly located in the northeastern part of the basin and in Awat County—being hotspots for high-arsenic water. Factors such as a weak reducing environment, intense evaporation, strong cation exchange, and the low-permeability recharge of surface water contribute to the accumulation of arsenic in the basin's groundwater. The results of this study are vital for assessing the risk of arsenic contamination in groundwater in similar basins and for identifying critical areas for further investigation and research.

**Keywords:** arsenic anomaly; Aksu River basin; geostatistics; Kriging interpolation method; cumulative frequency



**Citation:** Shao, F.; Wang, W.; Lu, Q.; Che, K.; Zhu, B. Spatial Distribution of Arsenic in the Aksu River Basin, Xinjiang, China: The Cumulative Frequency Curve and Geostatistical Analysis. *Sustainability* **2024**, *16*, 1697. <https://doi.org/10.3390/su16041697>

Academic Editor: Basu Bidroha

Received: 8 January 2024

Revised: 6 February 2024

Accepted: 7 February 2024

Published: 19 February 2024



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## 1. Introduction

Access to high-quality drinking water is crucial for maintaining human health and is a cornerstone of sustainable development [1,2]. Arsenic, a prevalent and harmful element found in groundwater, enters the human body through drinking water and food, posing significant health risks. Long-term consumption of arsenic-contaminated water and the consumption of fruits and vegetables irrigated with such water can lead to irreversible health effects [3,4]. The most common condition resulting from prolonged exposure is chronic arsenic poisoning. Alarmingly, continuous intake of arsenic can increase the risk of various organ cancers, including those of the liver and kidneys [5]. Data from The Global

Burden of Diseases, Injuries, and Risk Factors Study (GBD) 2019 Risk Factors Collaborators highlights that unsafe drinking water is a significant global risk factor, ranking 11th for females and 13th for males in causing deaths [6]. This emphasizes the need for increased vigilance and protective measures regarding drinking water safety to mitigate the health risks associated with arsenic contamination [3,5,6].

According to statistics, to date, high arsenic groundwater has been discovered in more than 70 countries worldwide, affecting a population of 94 million to 220 million people [7]. The majority of affected individuals, about 94%, are located in Asia, primarily in the river and lake basins or river delta regions of arid or semi-arid climates [7,8]. Examples of such regions include the Ganges Basin in India and the Red River Delta in Vietnam [9–13], the Bengal Basin in Bangladesh [14,15], and the Hetao Basin in the Yellow River Basin in China [16–18]. In recent years, with the reporting of research findings in this field, groundwater pollution has received significant attention from researchers as well as decision-makers in various governments.

Arsenic, as a non-metallic harmful element, primarily exists in geological sediments and natural water bodies in the environment. It accumulates in various organisms through the food chain [19]. Existing research indicates that the arsenic content in the Earth's crust is relatively low, with an average concentration of 1.5 mg/kg, while the majority of natural water bodies have arsenic concentrations mostly below 1.0 µg/L [7,19]. With the development of the Second and Third Industrial Revolutions, human exploitation of natural resources has increased significantly and become more refined.

Currently, over 200 naturally occurring minerals containing arsenic are known to exist [20,21]. Due to the development of mining industries, unquantifiable harmful elements, including arsenic, have transitioned from stable states to active states, entering the natural cycling system [22]. They undergo processes such as leaching, dissolution, evaporation concentration, and the cycling of the food chain, leading to iterative enrichment [23,24]. With a development philosophy centered around people's health, both China and the World Health Organization (WHO) have established and adopted safe guideline values for arsenic content in drinking water (less than 10 µg/L) in 2006 and 2011, respectively [25,26].

While some researchers have speculated about the potential impacts of groundwater arsenic contamination in Xinjiang, China, the region's intricate terrain and geological makeup have historically rendered it a "black-box" for in-depth study [27]. Specifically, research has been notably scarce in the Aksu River basin, a critical area for both agriculture and industry in southern Xinjiang, which also boasts a dense population [28]. The inhabitants of this region depend heavily on the basin for their daily living and agricultural needs. Alongside China's rapid development, Xinjiang's industrial and agricultural sectors have seen significant growth and enhancement. Nevertheless, this progress has come at a cost, particularly in the form of relentless and widespread groundwater extraction, culminating in a marked deterioration of water quality, most notably in the downstream regions of the basin.

This study utilizes geostatistical Kriging interpolation, guided by the slope of cumulative frequency curves for arsenic content and major ion ratios in the study area's groundwater, to achieve three primary objectives: Firstly, to examine the hydrogeochemical processes and spatial distributions of arsenic across various groundwater types within the study area. Secondly, to introduce a methodology for pinpointing the spatial distributions of high arsenic contents by analyzing the cumulative frequency curves of ion ratios. And lastly, to explore the mechanisms behind arsenic enrichment in distinct regions, classified according to the slopes of various ion ratios.

## 2. Overview of the Study Area

### 2.1. Geographic Feature

The Aksu River is located in Aksu Prefecture, Xinjiang, China, and it belongs to the northern edge of the Tarim Basin. The overall terrain of the region is higher in the northwest and lower in the southeast. The highest elevation in the study area is 2759 m, located in the

northwest, which is a branch of the Tianshan Mountains called the Latajiayi Mountain. This mountain range extends in a northwesterly direction. The lowest elevation is a fluvial plain at 1100 m, located in the southern part of the study area, with a slope ranging from 1 to 3‰. The maximum elevation difference in the study area is 1659 m.

## 2.2. Hydrology and Meteorology

The Aksu River basin is characterized by a typical arid to semi-arid warm temperate continental climate. Within the study area, the annual average temperature and evaporation increase with decreasing terrain elevation, while precipitation increases with higher terrain elevation. The Aksu River is the main tributary of the Tarim River, accounting for 75% of its flow. The Aksu River is formed by the confluence of the Toshkan River (western branch) and the Kumalak River (northern branch) within Wensu County. After the confluence, it flows through Aksu City and eventually joins the Tarim River to the south. Both rivers originate from the western segment of the Tianshan Mountains, with water supply mainly originating from mountain precipitation and snowmelt (Figure 1).

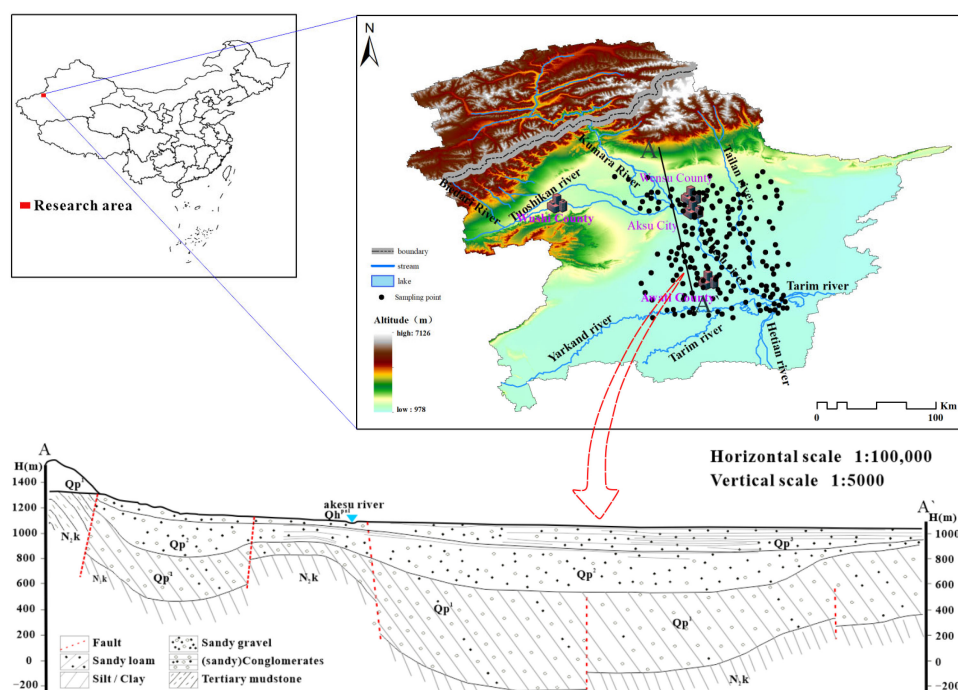


**Figure 1.** Spatial distribution of As and the sedimentary structure of the Aksu River basin.

## 2.3. Hydrogeological Condition

The Aksu River basin is characterized by the presence of thick Quaternary unconsolidated sediments, with a deposition thickness ranging from 1000 to 1500 m in the alluvial plain. In the piedmont alluvial fan area of the basin, the particle size of the Quaternary sediments gradually decreases from the piedmont towards the front edge of the alluvial plain. The lithology of the Quaternary sediments in the upper part of the alluvial plain is composed of conglomerates and gravel, while the middle part consists of gravel and coarse sand. The lower part of the alluvial plain is composed of fine sand, silt, silty clay, and clayey silt. In the Tarim River alluvial plain, the Quaternary sediments are mainly composed of fine sand, silt, silty clay, and clayey silt.

## 3. Materials and Methods

### 3.1. Sample Collection and Analysis

A total of 196 groundwater samples were collected with the assistance of the First Regional Geological Survey Brigade of the Xinjiang Uygur Autonomous Region Geology

and Mineral Exploration and Development Bureau. Each groundwater sample was taken from below 0.5 m below of the groundwater surface, with the location of each sample recorded using GPS technology. Groundwater was collected from each site in duplicate, stored in plastic bottles with airtight caps, and labelled appropriately. Membrane filtration (0.45  $\mu\text{m}$ ) of all samples was conducted on site. One of the duplicate samples was acidified on site using 2–3 drops of concentrated nitric acid ( $\text{HNO}_3$ , 69%, Electron-grade) to ensure a pH value lower than 2 and to stabilize arsenic and metal ions and prevent their precipitation. This acidified water sample was subsequently used to analyze the total arsenic content and other elements. The second duplicate sample, which was not acidified, was utilized to analyze various cations and anions. All samples were transported to the laboratory at 4  $^{\circ}\text{C}$ , and analyzed within 7 days.

The water temperature, pH and total dissolved solids (TDS) were tested using a sensION+MM150 (MM156) portable multi-parameter water quality analyzer produced by HACH Company on the sampling day, and the turbidity was tested using a WGZ-200B portable turbidimeter (meter) produced by the Shanghai Xingrui Company. At the laboratory of the School of Resources and Geosciences, China University of Mining and Technology, the arsenic content in groundwater was measured via inductively coupled plasma–mass spectroscopy (ICP-MS) (7500C, Agilent, Santa Clara, CA, USA).  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and other cations were measured via inductively coupled plasma–atomic emission spectroscopy (ICP-AES) and inductively coupled plasma–mass spectroscopy (ICP-MS). Anions ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) were analyzed using ICS1500 (Dionex, Sunnyvale, CA, USA), and  $\text{HCO}_3^-$  was determined via titration. The concentration errors of both cations and anions in all samples were within a range of less than 5%, ensuring the accuracy of all the data.

### 3.2. The Partition Method of Cumulative Frequency Curve

Cumulative frequency profiles have been proved to be a valuable tool for characterizing distributions, providing a visual indication of the cumulative distribution of different hydrogeochemical component ratios [29,30]. With the increases in both the ratio and the number of samples, the cumulative frequency gradually increased from 0% to 100%. Depending on the point of inflection, i.e., the point showing significant changes in the ratios, all data are represented by multiple straight lines with different slopes. These changes in slope reflect variations in the groundwater environment and hydrogeochemical processes. In this study, cumulative frequency curves of ion ratios were plotted and used in conjunction with geostatistical Kriging interpolation to clarify differences in the hydrogeochemical compositions of groundwater samples and reveal specific chemical processes in groundwater across different regions.

## 4. Results

### 4.1. Hydrogeochemical Distribution of Samples

The concentrations of ions and TDS in the 196 samples range from two to four orders of magnitude, indicating strong spatial variability in the groundwater (Table 1). Specifically, the pH of the groundwater in the Aksu River basin was neutral to weakly alkaline, ranging from 7.05 to 8.88, with a mean value of 8.15. The highest concentrations of anions and cations were  $\text{Cl}^-$  and  $\text{Na}^+$ , respectively, with median values of 266 and 197 mg/L. The TDS content ranged between 200 and 27,024 mg/L, with a median value of 1234 mg/L; brine (TDS > 1000 mg/L) accounted for 53.6%.

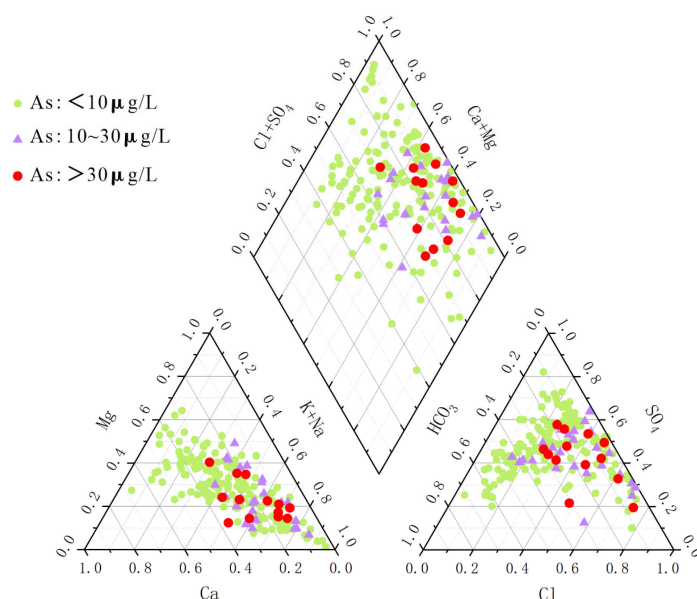
The Piper diagram revealed that the hydrogeochemical type of groundwater in the study area consists of  $\text{Na-HCO}_3\cdot\text{Cl}$  and  $\text{Na-HCO}_3(\text{SO}_4)$ , while the chemical type in the pre-mountain area and the middle and lower reaches of the river alluvial plain in the plain area of Aksu region is  $\text{Na-HCO}_3\cdot\text{SO}_4$ . The chemistry of high arsenic groundwater is mainly of the  $\text{Na-SO}_4\text{-Cl}$  type.

**Table 1.** Distribution of main ion concentrations in groundwater.

|                               | Units | Min. | Max.   | Ave. | Md   | S.E. | S.D. |
|-------------------------------|-------|------|--------|------|------|------|------|
| pH                            | --    | 7.05 | 8.88   | 8.15 | 8.24 | 0.03 | 0.39 |
| Ca <sup>2+</sup>              | mg/L  | 16.5 | 944    | 183  | 100  | 14.3 | 200  |
| Mg <sup>2+</sup>              | mg/L  | 4.90 | 1062   | 131  | 67.1 | 11.5 | 162  |
| Na <sup>+</sup>               | mg/L  | 17.4 | 8337   | 666  | 197  | 97.4 | 1364 |
| K <sup>+</sup>                | mg/L  | 0.98 | 114    | 16.4 | 7.05 | 1.50 | 21.0 |
| Cl <sup>−</sup>               | mg/L  | 18.9 | 11,504 | 918  | 266  | 139  | 1948 |
| SO <sub>4</sub> <sup>2−</sup> | mg/L  | 40.6 | 8363   | 910  | 382  | 87.3 | 1222 |
| HCO <sub>3</sub> <sup>−</sup> | mg/L  | 21.4 | 757    | 219  | 186  | 9.56 | 134  |
| CO <sub>3</sub> <sup>2−</sup> | mg/L  | 0    | 72.0   | 14.5 | 12.0 | 0.67 | 9.39 |
| TDS                           | mg/L  | 200  | 27,024 | 2916 | 1234 | 333  | 4668 |
| As                            | µg/L  | 0.05 | 210    | 8.70 | 2.05 | 1.53 | 21.5 |

Min.—minimum value; Max.—maximum value; Ave.—average value; Md—median; S.E.—standard error; S.D.—standard deviation.

In high arsenic groundwater, sodium (Na<sup>+</sup>) concentrations vary between 41.0 and 7532 mg/L (median: 280 mg/L), bicarbonate (HCO<sub>3</sub><sup>−</sup>) between 21.4 and 488 mg/L (median: 143 mg/L), calcium (Ca<sup>2+</sup>) from 20.7 to 943 mg/L (median: 89.2 mg/L), and magnesium (Mg<sup>2+</sup>) from 17.4 to 8337 mg/L (median: 197 mg/L). Total dissolved solids (TDS) range from 236 to 27,024 mg/L, with median and mean values of 1326 and 3672 mg/L, respectively. These values indicate a high level of salinization in arsenic-rich groundwater, particularly in groundwater with arsenic concentrations exceeding 30 µg/L, where the dominant hydrogeochemical type is Na-SO<sub>4</sub>-Cl (Figure 2).

**Figure 2.** Piper diagram of shallow groundwater in the study area.

#### 4.2. Spatial Distribution of Arsenic

The total arsenic concentration in groundwater ranged from 0.05 to 210 µg/L, with a mean value of 8.70 µg/L and a median value of 2.05 µg/L (Table 1). High arsenic (As > 10 µg/L) groundwater accounted for 19.4% of the total. To further understand the distribution of arsenic in groundwater in different geomorphological units, the 196 groundwater samples were divided into three groups based on arsenic concentrations (i.e., 0–10 µg/L, 10–30 µg/L, and >30 µg/L), and raw data were analyzed using ArcGIS.

### 4.3. Cumulative Frequency Curves and Distribution Characteristics of Ion Ratios

#### 4.3.1. $(\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-}$

In reducing environments in arid and semi-arid regions, sulfate is converted into sulfide ( $\text{S}^{2-}$ ) via microbial reactions, and the concentration of bicarbonate ( $\text{HCO}_3^-$ ) increases through the oxidative conversion of organic compounds [31]. In such climates, the  $(\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-}$  ratio increases with increasing groundwater reducibility, making it an indicator of the groundwater redox state. Based on changes in the slope variation in the cumulative frequency curve for the  $(\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-}$  ratio, the study area was divided into five zones: ① (0–0.57), ② (0.57–1.13), ③ (1.13–1.70), ④ (1.70–2.83) and ⑤ (>2.83) (Figure 3a). Zone ① is mainly distributed in the areas of the Duolanghu Reservoir and Xinjingzi Reservoir. Zones ② and ③ have the widest distribution area, with ② mainly being the area where the Aksu River, Yarkant River, and Hotan River converge with the Tarim River, and Zone ③ mainly being mainly distributed downstream of the Kumala River and Taushgan Darya, extending to Aksu City. Zones ④ and ⑤ are mainly distributed in parts of Aksu City and Onsu County near the Aksu River basin (Figure 4a).

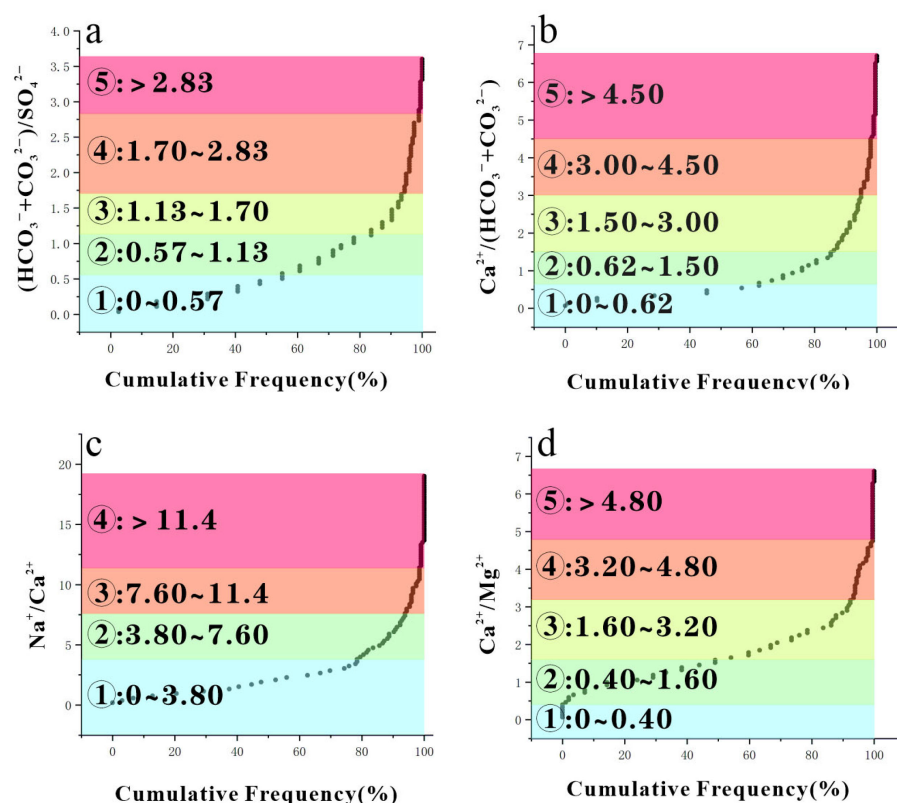


**Figure 3.** Cumulative frequency curves for  $(\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-}$  (a),  $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-})$  (b),  $\text{Na}^+/\text{Ca}^{2+}$  (c),  $\text{Ca}^{2+}/\text{Mg}^{2+}$  (d).

The majority of groundwater samples in the study area exhibited  $(\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-} < 2.83$ , and the arsenic concentration was found to be positively correlated with the ratio, so the groundwater in this area is a weakly reducing environment overall. The results of sample tests suggest that such an environment is influenced by the weakly reducing conditions.

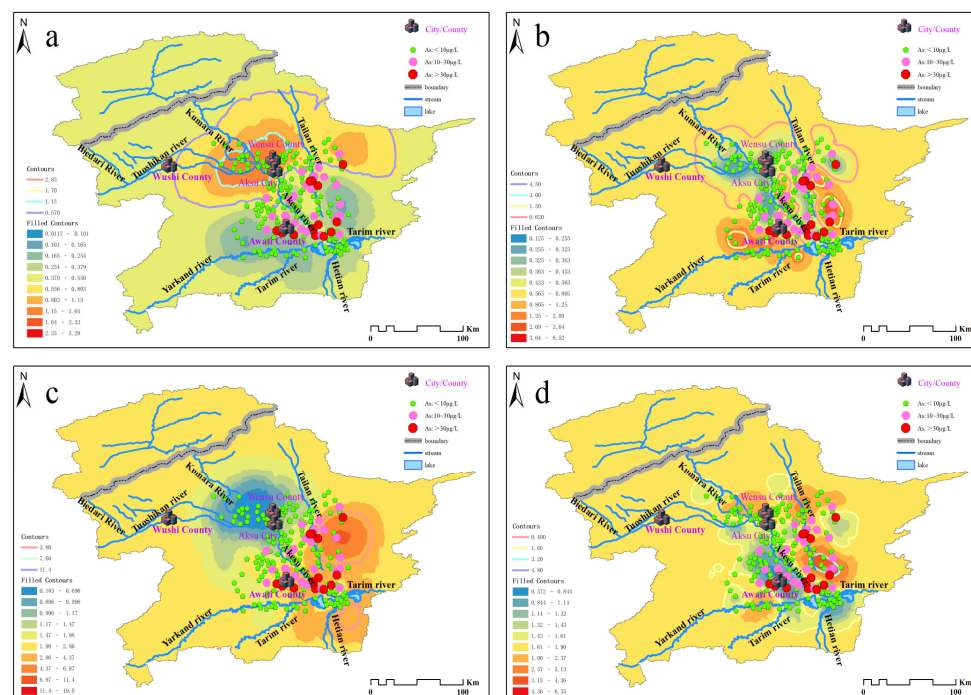


**Figure 4.** Spatial distribution of cumulative frequency.

#### 4.3.2. $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-})$

The concentration of  $\text{Ca}^{2+}$  in groundwater can serve as an indicator of the degree to which surface water is recharging the groundwater [17]. Moreover, the increase in the  $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-})$  ratio can be attributed to the dissolution of silicate minerals [32]. The ratio is significantly influenced by the mixing of surface water with groundwater or rainfall, as well as cation exchange. A higher ion ratio indicates stronger cation exchange and lower mixing ratios of surface water or rainfall. The correlation between arsenic levels and the  $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-})$  ratio was positive for the study area, with a greater correlation for high arsenic groundwater than for all samples combined. The study area was classified into five zones (①, ②, ③, ④, and ⑤) based on the slope variation in the cumulative frequency curve for  $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-})$  ratio (Figure 3b). Zone ① (0–0.62) was predominantly found in the upper reaches of the Aksu River, as well as in parts of Aksu City and Onsu County near the Aksu River basin. Zone ② (0.62–1.50) had the widest distribution area and was found in areas outside of the other groups. Zone ③ (1.50–3.00) was mainly distributed in the areas of the Duolanghu Reservoir, the Xinjingzi Reservoir, and the confluence area of the Yarkant River and Tarim River. Zones ④ (3.00–4.50) and ⑤ (>4.50) were mainly distributed in the downstream area of the Tailan River, i.e., parts of the Duolanghu Reservoir (Figure 4b).

For most of the underground samples,  $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-}) > 0.62$ , suggesting weak surface water recharge and strong cation exchange. The enrichment of arsenic in the groundwater may also be related to these factors.

#### 4.3.3. $\text{Ca}^{2+}/\text{Mg}^{2+}$

In different lithological aquifers, dissolution and leaching can result in  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio differences. As the ratio approaches 1 to 2, groundwater is primarily dissolved by carbonates such as calcite and dolomite, while a further increase in the ratio reflects the fact that the leaching of silicate minerals also played a role [33]. Therefore, the  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio reflects the intensity of lateral recharge, as an increase in the former can indicate an enhancement of the latter. The study area was divided into four zones, labeled ①, ②, ③, and ④, according to the slope change in the  $\text{Ca}^{2+}/\text{Mg}^{2+}$  cumulative frequency curve (Figure 3c). Zone ① (0–3.80) is mainly distributed in the upper reaches of the Aksu River and part of

the lower reaches of the Kumala and Taushgan Darya rivers, specifically parts of Aksu City and Onsu County near the Aksu River basin. Zone ② (3.80–7.60) has a narrower distribution range and is mainly distributed in the periphery of Zone. Zones ③ (7.60–11.4) and ④ (>11.4) have the widest distribution area, including the upper reaches of the Kumala River basin, the lower reaches of the Taushgan Darya, the upper reaches of the Tailan River, and parts of the Yarkant and Tarim River basins in China (Figure 4c).

In the study area, there are 51 samples (26%) with  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratios between 1 and 2, and 97 groups (49.5%) with  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratios exceeding 2. This suggests that the dissolution of carbonates such as calcite and dolomite, as well as the leaching of silicate minerals, is affecting the region.

#### 4.3.4. $\text{Na}^+/\text{Ca}^{2+}$

Poor local runoff conditions can lead to cation exchange between groundwater and aquifer minerals. The  $\text{Na}^+/\text{Ca}^{2+}$  ratio can be used to evaluate the extent of cation exchange in groundwater [34]. As cation exchange intensifies, the Na content and  $\text{Na}^+/\text{Ca}^{2+}$  ratio gradually increase. Based on the  $\text{Na}^+/\text{Ca}^{2+}$  cumulative probability curve, the study area can be classified into five zones and labeled as ①, ②, ③, ④, and ⑤ (Figure 3d). Zone ① (0–0.40) is primarily located within Awat County and the region stretching from the confluence of the Hotan River to the Tarim River. Zone ② (0.40–1.60) has a scattered distribution, mainly in the vicinity of Aksu City, as well as the Dolanghu Reservoir and Xinjingzi Reservoir areas. Zone ③ (1.60–3.20) has the broadest distribution and is present in areas other than those covered by the other groups. Zone ④ (3.20–4.80) is situated in the upper basin of the Tailan River, part of Onsu County that is close to the Kumala River basin, and in portions of Awat County near the Yarkant River basin. Zone ⑤ (>4.80) is primarily distributed in the lower reaches of the Tailan River, including the Dolanghu reservoir area (Figure 4d).

## 5. Discussion

### 5.1. Relationship between Different Ion Ratios and Spatial Distribution of Arsenic

Hydrogeochemical processes in the groundwater environment are the primary drivers of arsenic presence. The spatial distribution of different ion ratios is key to identifying these processes and the mechanisms of arsenic distribution in the study area. By analyzing the concentration characteristics and spatial distributions of these ion ratios, the final boundaries of each zone are determined using geostatistical techniques, including kriging interpolation. This approach delineates five distinct zones (I–V) (Figure 5).

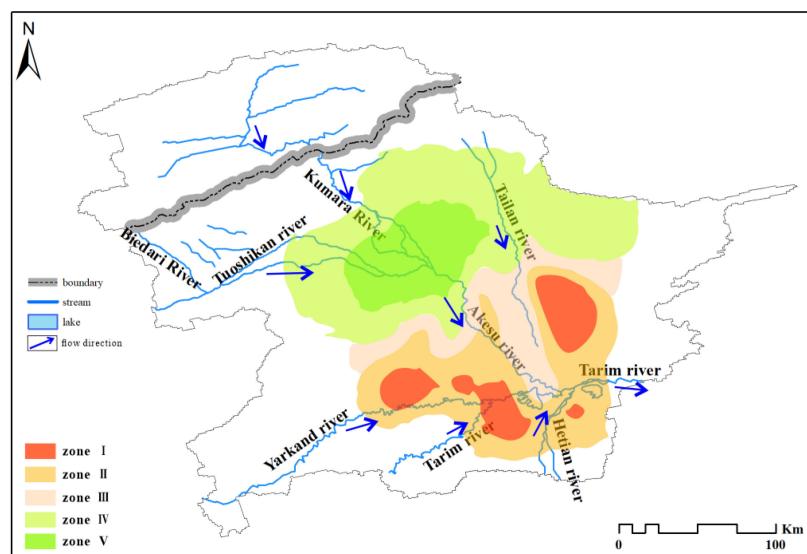


**Figure 5.** Ion ratio distribution and regional recognition in groundwater.

Zone I was characterized by  $0.01 < (\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-} < 0.4$ ,  $0.43 < \text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-}) < 6.52$ ,  $0.09 < \text{Ca}^{2+}/\text{Mg}^{2+} < 11.5$ ,  $0.60 < \text{Na}^+/\text{Ca}^{2+} < 6.35$ . Zone I is more sporadically distributed, mainly in Xinjingzi Reservoir and Awat County (Figure 5), where the concentrations of  $\text{Na}^+$  (mean and median: 2097 and 550 mg/L),  $\text{Ca}^{2+}$  (483 and 519 mg/L), and  $\text{Mg}^{2+}$  (353 and 219 mg/L) are the highest among the five areas (Figure 6a–c). In zone I, The concentrations of  $\text{HCO}_3^-$  (mean and median: 308 and 275 mg/L),  $\text{SO}_4^{2-}$  (4157 and 5240 mg/L) and  $\text{Cl}^-$  (7715 and 6541 mg/L) are the highest among the five zones (Figure 6d–f). The mean and median arsenic concentrations in the area are 6.49 and 2.34  $\mu\text{g/L}$ , respectively, and the majority of samples in the area had arsenic concentrations of less than 10  $\mu\text{g/L}$  (82.4%) (Figure 7). Overall, the area appears to be in a weakly reducing, strong lateral/surface water recharge, and moderate cation exchange environment (Table 2).

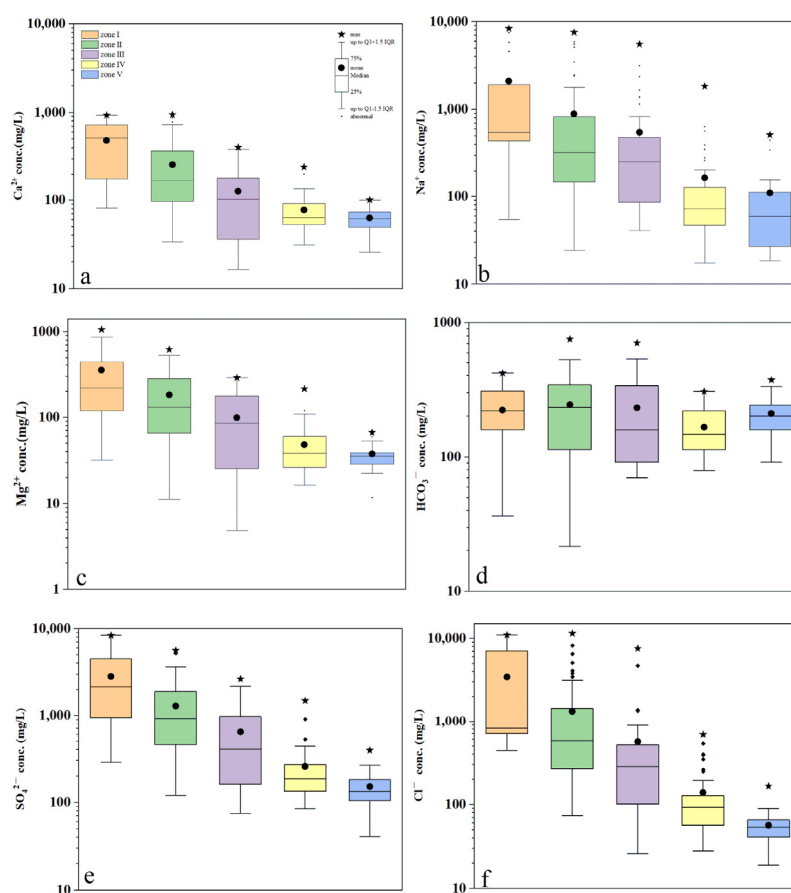


**Figure 6.** Main ions-box plot of different intensity zones in aquifers.

Zone II is characterized by  $0.03 < (\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-} < 1.35$ ,  $0.22 < \text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-}) < 4.5$ ,  $0.08 < \text{Ca}^{2+}/\text{Mg}^{2+} < 35.19$ ,  $0.37 < \text{Na}^+/\text{Ca}^{2+} < 4.32$ . Zone II is located in the lower reaches of the Aksu River basin and the alluvial flood plain in the confluence basin of Aksu River, Yarkant River and Tarim River (Figure 5), for which the concentrations of  $\text{Na}^+$  (mean and median: 661 and 302 mg/L),  $\text{Ca}^{2+}$  (238 and 165 mg/L), and  $\text{Mg}^{2+}$  (171 and 128 mg/L) (Figure 6a–c). It shows that the cation exchange capacity in this area is medium, and the groundwater runoff condition is general. The mean and median arsenic concentrations in the area are 10.51 and 3.97  $\mu\text{g/L}$ , and in most samples, the value is smaller than 10  $\mu\text{g/L}$  (Figure 7).

Zone III is characterized by  $0.13 < (\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-} < 0.49$ ,  $0.17 < \text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-}) < 1.54$ ,  $0.21 < \text{Ca}^{2+}/\text{Mg}^{2+} < 36.2$ ,  $0.53 < \text{Na}^+/\text{Ca}^{2+} < 4.6$ . Zone III is located in the transition area between zones II and VI (Figure 5), for which the concentrations of  $\text{Na}^+$  (mean and median: 549 and 254 mg/L),  $\text{Ca}^{2+}$  (126 and 102 mg/L), and  $\text{Mg}^{2+}$  (99 and 86 mg/L) (Figure 6a–c). This indicates a continuous weakening of the region's cation exchange capacity and a decline in groundwater runoff conditions. The mean and median arsenic concentrations

in this zone are 15.15  $\mu\text{g/L}$  and 4.11  $\mu\text{g/L}$ , respectively. Most of the samples have arsenic concentrations of less than 10  $\mu\text{g/L}$  (75.5%), and the most abnormal arsenic concentration (210  $\mu\text{g/L}$ ) detected in this study is located in this zone (Figure 7).

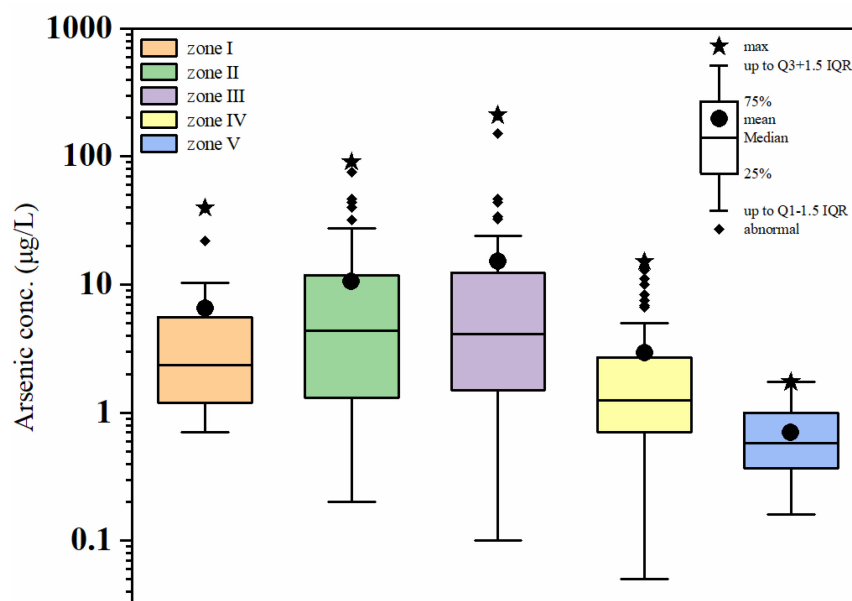


Figure 7. Box plot of arsenic concentration in different zones.

Table 2. The meaning of different ion ratios and the distribution of the arsenic concentration.

| Ion Ratio                                              | Distribution Range        | Implication                                     | Arsenic Concentration ( $\mu\text{g/L}$ ) |      | Proportion of High Arsenic |
|--------------------------------------------------------|---------------------------|-------------------------------------------------|-------------------------------------------|------|----------------------------|
|                                                        |                           |                                                 | Md                                        | Ave  |                            |
| $(\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-}$ | $<2$ ( $n = 188$ )        | Weak reduction environment                      | 2.2                                       | 8.96 | 97.37%                     |
|                                                        | $>2$ ( $n = 8$ )          | Medium reduction environment                    | 0.65                                      | 2.64 | 2.63%                      |
|                                                        |                           | Medium lateral/surface water recharge intensity | 1.9                                       | 9.49 | 57.89%                     |
| $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-})$   | $<0.7$ ( $n = 127$ )      | Strong lateral/surface water recharge intensity | 2.24                                      | 7.25 | 42.11%                     |
|                                                        | $>0.7$ ( $n = 69$ )       | Weak cation exchange                            | 0.85                                      | 2.59 | 2.63%                      |
|                                                        |                           | Medium cation exchange                          | 3.3                                       | 11.4 | 94.74%                     |
| $\text{Ca}^{2+}/\text{Mg}^{2+}$                        | $<1.1$ ( $n = 54$ )       | Strong cation exchange                          | 19                                        | 22.3 | 2.63%                      |
|                                                        | $1.1\sim13$ ( $n = 133$ ) | Weak lateral recharge intensity                 | 4.35                                      | 4.35 | 0.00%                      |
|                                                        | $>13$ ( $n = 9$ )         | Medium lateral recharge intensity               | 3.3                                       | 12.2 | 50.00%                     |
| $\text{Na}^+/\text{Ca}^{2+}$                           | $<0.4$ ( $n = 1$ )        | Strong lateral recharge intensity               | 1.74                                      | 6.16 | 50.00%                     |
|                                                        | $0.4\sim1.4$ ( $n = 83$ ) |                                                 |                                           |      |                            |
|                                                        | $>1.4$ ( $n = 112$ )      |                                                 |                                           |      |                            |

Zone IV is characterized by  $0.01 < (\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-} < 0.4$ ,  $0.43 < \text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-}) < 6.52$ ,  $0.09 < \text{Ca}^{2+}/\text{Mg}^{2+} < 11.5$ ,  $0.60 < \text{Na}^+/\text{Ca}^{2+} < 6.35$ . Zone IV encompasses the upper reaches of Kumala and Taushgan Darya rivers, as well as part of the upper Aksu River area, covering the most extensive area (Figure 5), for which the concentrations of  $\text{Na}^+$  (mean and median: 2097 and 550  $\text{mg/L}$ ),  $\text{Ca}^{2+}$  (483 and 519  $\text{mg/L}$ ), and  $\text{Mg}^{2+}$  (353 and 219  $\text{mg/L}$ ) (Figure 6a–c). They show that the cation exchange capacity in this area is weak and the groundwater runoff condition is poor (Table 2). The mean and median arsenic concentrations in this area are 2.95  $\mu\text{g/L}$  and 1.24  $\mu\text{g/L}$ , respectively, with most samples being less than 10  $\mu\text{g/L}$  (Figure 7).

Zone V is characterized by  $0.51 < (\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-} < 3.29$ ,  $0.12 < \text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-}) < 0.55$ ,  $0.22 < \text{Ca}^{2+}/\text{Mg}^{2+} < 19.79$ ,  $0.74 < \text{Na}^+/\text{Ca}^{2+} < 2.95$ . Zone V is located in the upper reaches of the Aksu River, within Aksu City and Onsu County (Figure 5), where the concentrations of  $\text{Na}^+$  (mean and median: 110 and 58.96  $\text{mg/L}$ ),  $\text{Ca}^{2+}$  (62.68 and 61.80  $\text{mg/L}$ ), and  $\text{Mg}^{2+}$  (37.64 and 35.64  $\text{mg/L}$ ) are the lowest among the five areas (Figure 6a–c), indicating weak cation exchange and slow groundwater runoff in this area (Table 2). The mean and median arsenic concentrations in this area are 0.70 and 0.58  $\mu\text{g/L}$ . This area has the lowest arsenic content as the concentration for all samples are below 10  $\mu\text{g/L}$  (Figure 7).

In the study area, Zone I exhibits the lowest  $(\text{HCO}_3^- + \text{CO}_3^{2-})/\text{SO}_4^{2-}$  ratio, indicating the highest degree of groundwater oxidation [35]. This finding suggests the possible influence of neighboring surface water quality on groundwater. The mixing of groundwater with surface water containing higher oxygen levels may result in increased groundwater oxidation. Moreover, the smallest  $\text{Na}^+/\text{Ca}^{2+}$  ratio in Zone V implies weak cation exchange between  $\text{Ca}^{2+}$  and  $\text{Na}^+$  within the aquifer and favorable runoff conditions.

As the topographic gradient declines from Zone V to I, groundwater runoff slows, and sediment becomes finer. This slowdown, combined with enhanced evaporation and water mineralization, leads to groundwater discharge mainly through evaporation, lateral runoff, and human extraction, diminishing river recharge. Arsenic concentrations in groundwater are highest in Zone III and lowest in Zone V, with zones II and III showing similar levels.

The areas experiencing abnormal arsenic enrichment are predominantly located in the northeastern part of the basin and in Awat County. Specifically, in the northeast, unsafe arsenic levels are primarily found between the Tailan River and the Karayulgun River, influenced by the stratigraphy of upstream outflows. In the northern sector, the terrain is steep with coarse sandy gravel, facilitating good water runoff. However, moving southward, the geological composition transitions to finer materials such as clay, mud, fine sand, and silty sand, resulting in poorer runoff conditions. This region's history of frequent marsh formation has led to a high content of organic matter, including humus, which acts as a significant source for arsenic accumulation. Additionally, the combination of flat terrain and intense evaporation further exacerbates arsenic concentrations in the groundwater.

Awat County, on the other hand, is an alluvial-lacustrine deposit soil plain with flat topography, featuring a slope of less than 1‰. Slow groundwater runoff often results in the formation of wet-sinking depressions on the surface. A series of factors, including poor water flow, strong evaporation, saline development, and long-term sediment saturation, can promote the release of arsenic from the sediments into the water and leads to a groundwater anomaly that is high with arsenic concentrations.

## 5.2. Hydrogeochemical Processes

Worldwide, high arsenic levels in groundwater are often accompanied by high  $\text{HCO}_3^-$  concentrations [10,15,17]. Hence,  $\text{HCO}_3^-/\text{SO}_4^{2-}$  can indicate the degree of reducing conditions in the study area, a key factor in groundwater arsenic enrichment. Groundwater samples with lower arsenic levels typically have  $\text{HCO}_3^-/\text{SO}_4^{2-}$  ratios greater than 1, whereas samples with higher arsenic levels often show ratios less than 1. The concentration of groundwater arsenic is positively associated with  $\text{HCO}_3^-/\text{SO}_4^{2-}$ , which suggests that a weakly reducing environment plays a major role in generating the high concentrations of arsenic (Figures 6d,e and 8a).

Aside from reducing conditions, the high arsenic groundwater in the study area may also be related to the evaporative concentration. Due to its high solubility,  $\text{Cl}^-$  is difficult to be removed from the groundwater environment, and the only way increase its concentration is through the dissolution of rock minerals in the aquifer.  $\text{SO}_4^{2-}$  is often considered to be a sensitive component of redox conditions, and  $\text{Cl}^-/\text{SO}_4^{2-}$  can indicate the degrees of both the environmental redox and the groundwater evolution [36]. The high-arsenic groundwater in the study area has  $\text{Cl}^-/\text{SO}_4^{2-} > 1$  (47.4%) (Figures 6e,f and 8b), showing a weak oxidation environment.

$\text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-})$  reflects the extent to which Ca- $\text{HCO}_3$  type surface water recharges groundwater [37]. The higher the ionic ratio, the stronger the cation exchange and the lower the ratio of surface water or rainfall mixing. Strong surface water/rainfall recharge is typically present in zones IV and V of the study area (Figures 6a–d and 8c). In contrast, the weakest lateral/surface water recharge effect is present in zones I and II, along with strong cation exchange. Weak recharge and strong cation exchange may also be associated with arsenic enrichment in groundwater in this study area.

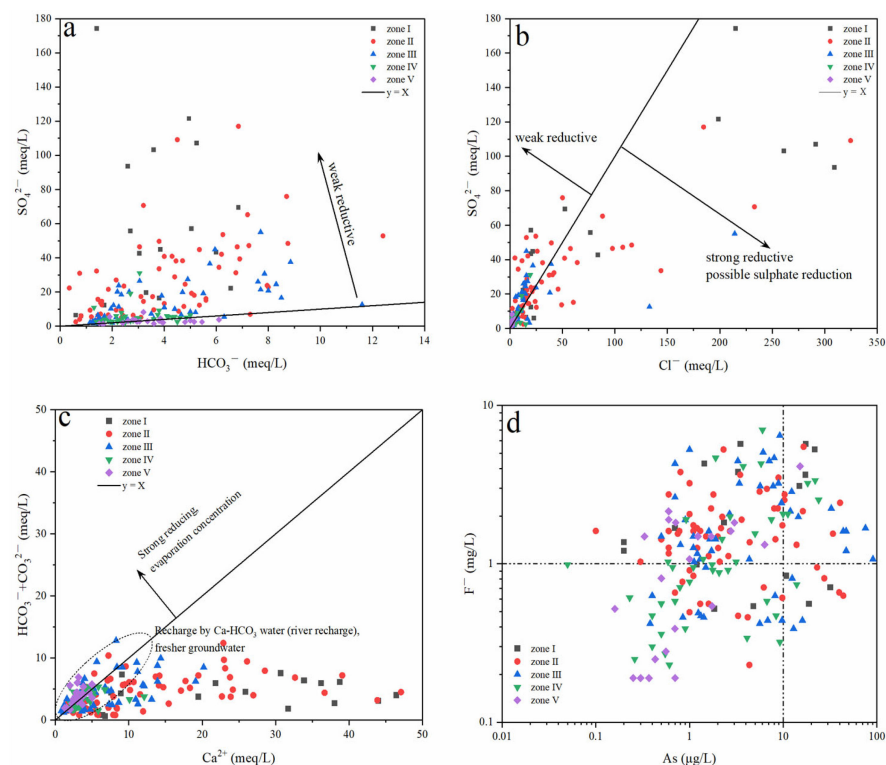


**Figure 8.** Relationship between the major ionic against a 1:1 equivalence ratio (a–c). (a),  $\text{HCO}_3^-/\text{SO}_4^{2-}$  ratio; (b),  $\text{Cl}^-/\text{SO}_4^{2-}$  ratio; (c)  $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{CO}_3^{2-})$  ratio; (d), correlation between  $\text{F}^-$  and As in this study area.

No significant correlation between  $\text{F}^-$  and As was found in the study area (Figure 8d). Highly fluorinated groundwater is mainly distributed in Zones III and IV, where the  $\text{Na}^+$  content is high. High  $\text{Ca}^{2+}$  is not conducive to fluoride enrichment, as  $\text{Ca}^{2+}$  and  $\text{F}^-$  in groundwater can form fluorite precipitates. The enrichment of arsenic in Zones III and IV is facilitated by the shallow groundwater levels and significant evaporative concentration within the study area. However, the release of arsenic into groundwater is hindered in Zone V due to weak runoff and oxidizing environments. The characteristics and ion ratios in Zone IV indicate that the conditions in this transition zone are conducive to the release of arsenic (Figure 9).

The analysis of arsenic concentration and its spatial distribution within the study area indicates that the depositional environment plays a significant role in influencing arsenic levels. Notably, high arsenic concentrations in groundwater appear sporadically, primarily in the eastern part of the region. The Aksu area, characterized by an arid to semi-arid inland climate, experiences low rainfall and high evaporation rates, where evaporation surpasses precipitation. In zones of arsenic enrichment, the groundwater table is notably high, leading to predominantly vertical rather than lateral water flow. These conditions, along with intense weathering processes, accelerate decomposition rates and biogeochemical cycles, creating conducive conditions for arsenic migration and accumulation. Arsenic is mobilized from arsenic-rich soil particles and organic matter into the groundwater, where it becomes concentrated due to ongoing evaporation. Significant arsenic levels were detected in groundwater at various locations, including Awat County, Kezile Township, Kezile Kumu Village, and Gulawati Township. Notably, water samples from the vicinity of the Dolanghu Reservoir exhibited extremely high arsenic levels, reaching up to  $210 \mu\text{g/L}$ , far exceeding the standard levels. Conversely, in several other regions, arsenic concentrations generally remain below  $10 \mu\text{g/L}$ .

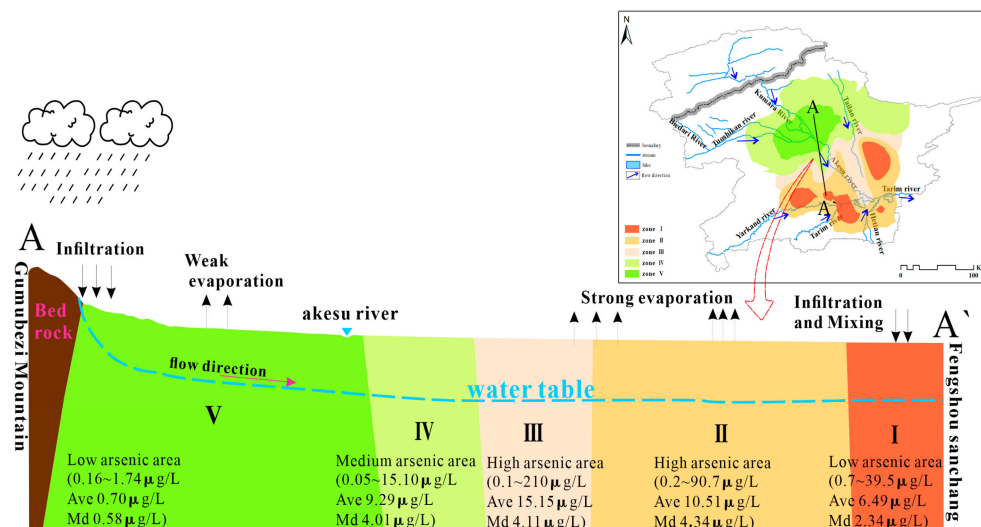


Figure 9. Hydrogeochemical model of groundwater in the study area.

## 6. Conclusions

This study explored the spatial distribution of arsenic within China's Aksu River basin by employing cumulative frequency curves and geostatistical analysis. It found a wide range in groundwater arsenic levels, with the most severe contamination in the northeast and Awat County, highlighting the strong spatial variability and significant correlation of arsenic concentration.

Geostatistical analysis enabled the classification of the study area into three zones: areas with high arsenic anomalies, areas with moderate arsenic levels, and areas with low arsenic presence. The high arsenic zones, mainly in zones II and III, are characterized by a weak reducing environment, gentle terrain slopes (less than 1‰), slow groundwater movement, strong cation exchange, and significant evaporation, coupled with limited surface water/rainwater recharge capacity. Zone IV corresponds to the moderate arsenic area, while zones I and V are identified as low arsenic zones. The process of arsenic migration is intricate, and its exact pathways remain partially understood. No single mechanism adequately accounts for the migration and accumulation of arsenic; a combination of processes provides a more plausible explanation for arsenic release into groundwater. This research significantly contributes to the assessment of arsenic contamination risks in similar hydrogeological settings and prioritizes areas for further investigation.

**Author Contributions:** Conceptualization, F.S. and Q.L.; methodology, F.S., Q.L., K.C. and B.Z.; formal analysis, F.S. and Q.L.; investigation, F.S., Q.L., K.C. and B.Z.; resources, W.W.; data curation, F.S. and Q.L.; writing—original draft preparation, F.S. and Q.L.; writing—review and editing, W.W.; supervision, W.W.; project administration, W.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was supported by the National Natural Science Foundation of China (No. U1903207), the Third Xinjiang Scientific Expedition Program (Grant No. 2022xjkk1003), and the Major Science and Technology Special Project of Xinjiang Uygur Autonomous Region (No. 2022A03014).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Acknowledgments:** We thank the editor and reviewers for their insightful comments.

**Conflicts of Interest:** The authors declare no competing interests.

## References

- Niazi, N.K.; Bibi, I.; Fatimah, A.; Shahid, M.; Javed, M.T.; Wang, H.; Ok, Y.S.; Bashir, S.; Murtaza, B.; Saqib, Z.A. Phosphate-assisted phytoremediation of arsenic by *Brassica napus* and *Brassica juncea*: Morphological and physiological response. *Int. J. Phytoremediat.* **2017**, *19*, 670–678. [\[CrossRef\]](#)
- Niazi, N.K.; Bibi, I.; Shahid, M.; Ok, Y.S.; Burton, E.D.; Wang, H.; Shaheen, S.M.; Rinklebe, J.; Lüttge, A. Arsenic removal by perilla leaf biochar in aqueous solutions and groundwater: An integrated spectroscopic and microscopic examination. *Environ. Pollut.* **2018**, *232*, 31–41. [\[CrossRef\]](#)
- Chen, Y.; Ahsan, H. Cancer burden from arsenic in drinking water in Bangladesh. *Am. J. Public Health* **2004**, *94*, 741–744. [\[CrossRef\]](#)
- Wu, R.H.; Xu, L.Q.; Polya, D.A. Groundwater Arsenic-Attributable Cardiovascular Disease (CVD) Mortality Risks in India. *Water* **2021**, *13*, 2232. [\[CrossRef\]](#)
- Sheng, D.; Wen, X.; Wu, J.; Wu, M.; Yu, H.J.; Zhang, C.Q. Comprehensive Probabilistic Health Risk Assessment for Exposure to Arsenic and Cadmium in Groundwater. *Environ. Manag.* **2021**, *67*, 779–792. [\[CrossRef\]](#) [\[PubMed\]](#)
- GBD 2019 Risk Factors Collaborators. Global burden of 87 risk factors in 204 countries and territories, 1990–2019: A systematic analysis for the global burden of disease study 2019. *Lancet* **2020**, *396*, 1223–1249. [\[CrossRef\]](#) [\[PubMed\]](#)
- Podgorski, J.; Berg, M. Global threat of arsenic in groundwater. *Science* **2020**, *368*, 845–850. [\[CrossRef\]](#) [\[PubMed\]](#)
- Benner, S.G.; Fendorf, S. Arsenic in South Asia Groundwater. *Geogr. Compass* **2010**, *4*, 1532–1552. [\[CrossRef\]](#)
- Ravindra, K.; Mor, S. Distribution and health risk assessment of arsenic and selected heavy metals in Groundwater of Chandigarh, India. *Environ. Pollut.* **2019**, *250*, 820–830. [\[CrossRef\]](#) [\[PubMed\]](#)
- Mukherjee, A.; Fryar, A.E.; Eastridge, E.M.; Nally, R.S.; Chakraborty, M.; Scanlon, B.R. Controls on high and low groundwater arsenic on the opposite banks of the lower reaches of River Ganges, Bengal basin, India. *Sci. Total Environ.* **2018**, *645*, 1371–1387. [\[CrossRef\]](#) [\[PubMed\]](#)
- Chakraborty, D.; Singh, S.K.; Rahman, M.M.; Dutta, R.N.; Mukherjee, S.C.; Pati, S.; Kar, P.B. Groundwater Arsenic Contamination in the Ganga River Basin: A Future Health Danger. *Int. J. Environ. Res. Public Health* **2018**, *15*, 180. [\[CrossRef\]](#) [\[PubMed\]](#)
- Huq, M.E.; Fahad, S.; Shao, Z.F.; Sarven, M.S.; Khan, I.A.; Alam, M.; Saeed, M.; Ullah, H.; Adnan, M.; Saud, S.; et al. Arsenic in a groundwater environment in Bangladesh: Occurrence and mobilization. *J. Environ. Manag.* **2020**, *262*, 110318. [\[CrossRef\]](#) [\[PubMed\]](#)
- Tareq, S.M.; Safiullah, S.; Anawar, H.M.; Rahman, M.M.; Ishizuka, T. Arsenic pollution in groundwater: A self-organizing complex geochemical process in the deltaic sedimentary environment, Bangladesh. *Sci. Total Environ.* **2003**, *313*, 213–226. [\[CrossRef\]](#)
- Neidhardt, H.; Rudischer, S.; Eiche, E.; Schneider, M.; Stopelli, E.; Duyen, V.T.; Trang PT, K.; Viet, P.H.; Neumann, T.; Berg, M. Phosphate immobilisation dynamics and interaction with arsenic sorption at redox transition zones in floodplain aquifers: Insights from the Red River Delta, Vietnam. *J. Hazard. Mater.* **2021**, *411*, 125128. [\[CrossRef\]](#)
- Stopelli, E.; Duyen, V.T.; Mai, T.T.; Trang PT, K.; Viet, P.H.; Lightfoot, A.; Kipfer, R.; Schneider, M.; Eiche, E.; Kontny, A.; et al. Spatial and temporal evolution of groundwater arsenic contamination in the Red River delta, Vietnam: Interplay of mobilisation and retardation processes. *Sci. Total Environ.* **2020**, *717*, 137143. [\[CrossRef\]](#) [\[PubMed\]](#)
- Ren, Y.; Cao, W.; Li, Z.Y.; Pan, D.; Wang, S. Identification of arsenic spatial distribution by hydrogeochemical processes represented by different ion ratios in the Hohhot Basin, China. *Environ. Sci. Pollut. Res.* **2023**, *30*, 2607–2621. [\[CrossRef\]](#)
- Cao, W.G.; Guo, H.M.; Zhang, Y.L.; Ma, R.; Li, Y.S.; Dong, Q.Y.; Li, Y.J.; Zhao, R.K. Controls of paleochannels on groundwater arsenic distribution in shallow aquifers of alluvial plain in the Hetao Basin, China. *Sci. Total Environ.* **2018**, *613*, 958–968. [\[CrossRef\]](#)
- Ke, T.T.; Zhang, D.; Guo, H.M.; Xiu, W.; Zhao, Y. Geogenic arsenic and arsenotrophic microbiome in groundwater from the Hetao Basin. *Sci. Total Environ.* **2022**, *852*, 158549. [\[CrossRef\]](#)
- Guo, H.M.; Wen, D.G.; Liu, Z.Y.; Jia, Y.F.; Guo, Q. A review of high arsenic groundwater in mainland and Taiwan, China: Distribution, characteristics and geochemical processes. *Appl. Geochem.* **2014**, *41*, 196–217. [\[CrossRef\]](#)
- Mandal, B.K.; Suzuki, K.T. Arsenic round the world: A review. *Talanta* **2002**, *58*, 201–235. [\[CrossRef\]](#)
- Smedley, P.L.; Kinniburgh, D.G. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **2002**, *17*, 517–568. [\[CrossRef\]](#)
- Rosas-Castor, J.M.; Portugal, L.; Ferrer, L.; Guzman-Mar, J.L.; Hernandez-Ramirez, A.; Cerda, V.; Hinojosa-Reyes, L. Arsenic fractionation in agricultural soil using an automated threestep sequential extraction method coupled to hydride generation-atomic fluorescence spectrometry. *Anal. Chim. Acta* **2015**, *874*, 1–10. [\[CrossRef\]](#)
- He, X.D.; Li, P.Y.; Ji, Y.J.; Wang, Y.H.; Su, Z.; Vetrimurugan, E. Groundwater arsenic and fluoride and associated arsenicosis and fluorosis in China: Occurrence, distribution and management. *Expo. Health* **2020**, *12*, 355–368. [\[CrossRef\]](#)
- Wang, Y.X.; Li, J.X.; Ma, T.; Xie, X.J.; Gan, Y.Q. Genesis of geogenic contaminated groundwater: As, F and I. *Crit. Rev. Environ. Sci. Technol.* **2020**, *51*, 2895–2933. [\[CrossRef\]](#)
- GB/T 5750.1-2006; Standard Examination Methods for Drinking Water—General Principles. Chinese Standard: Beijing, China, 2006.
- WHO (World Health Organization). *Guidelines for Drinking—Water Quality*, 4th ed.; WHO: Geneva, Switzerland, 2011.
- Rodríguez-Lado, L.; Sun, G.F.; Berg, M.; Zhang, Q.; Xue, H.; Zheng, Q.; Johnson, C.A. Groundwater arsenic contamination throughout China. *Science* **2013**, *341*, 866–868. [\[CrossRef\]](#) [\[PubMed\]](#)
- Wang, H.B.; Xu, J.M.; Gomez, M.A.; Shi, Z.L.; Li, S.F.; Zang, S.Y. Arsenic concentration, speciation, and risk assessment in sediments of the Xijiang River basin, China. *Environ. Monit. Assess.* **2020**, *191*, 56. [\[CrossRef\]](#) [\[PubMed\]](#)

29. Tennant, C.B.; White, M.L. Study of the distribution of some geochemical data. *Econ. Geol.* **1959**, *54*, 1281–1290. [[CrossRef](#)]
30. Sinclair, A.J. Selection of threshold values in geochemical data using probability graphs. *J. Geochem. Explor.* **1974**, *3*, 129–149. [[CrossRef](#)]
31. Guo, H.M.; Yang, S.Z.; Tang, X.H.; Li, Y.; Shen, Z.L. Groundwater geochemistry and its implications for arsenic mobilization in shallow aquifers of the Hetao Basin, Inner Mongolia. *Sci. Total Environ.* **2008**, *393*, 131–144. [[CrossRef](#)]
32. Gao, Z.J.; Han, C.; Xu, Y.; Zhao, Z.H.; Luo, Z.J.; Liu, J.T. Assessment of the water quality of groundwater in Bohai Rim and the controlling factors—A case study of northern Shandong Peninsula, north China. *Environ. Pollut.* **2021**, *285*, 117482. [[CrossRef](#)]
33. Asare, A.; Appiah-Adjei, E.K.; Ali, B.; Owusu-Nimo, F. Assessment of seawater intrusion using ionic ratios: The case of coastal communities along the central region of Ghana. *Environ. Earth Sci.* **2021**, *80*, 307. [[CrossRef](#)]
34. Li, C.C.; Gao, X.B.; Li, S.Q.; Bundschuh, J. A review of the distribution, sources, genesis, and environmental concerns of salinity in groundwater. *Environ. Sci. Pollut. Res.* **2020**, *27*, 41157–41174. [[CrossRef](#)] [[PubMed](#)]
35. Jessen, S.; Postma, D.; Larsen, F.; Nhan, P.Q.; Hoa, L.Q.; Pham, T.T.K.; Long, T.V.; Viet, P.H.; Jakobsen, R. Surface complexation modeling of groundwater arsenic mobility: Results of a forced gradient experiment in a Red River flood plain aquifer, Vietnam. *Geochim. Cosmochim. Acta* **2012**, *98*, 186–201. [[CrossRef](#)]
36. Sánchez-Martos, F.; Pulido-Bosch, A.; Molina-Sánchez, L.; Vallejos-Izquierdo, A. Identification of the origin of salinization in groundwater using minor ions (Lower Andarax, Southeast Spain). *Sci. Total Environ.* **2002**, *297*, 43–58. [[CrossRef](#)]
37. Montety, V.D.; Radakovitch, O.; Vallet-Coulomb, C.; Blavoux, B.; Hermitte, D.; Valles, V. Origin of groundwater salinity and hydrogeochemical processes in a confined coastal aquifer: Case of the Rhône delta (southern France). *Appl. Geochem.* **2008**, *23*, 2337–2349. [[CrossRef](#)]

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