



# Source, migration, distribution, toxicological effects and remediation technologies of arsenic in groundwater in China

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## ABSTRACT

Groundwater with high arsenic (As) content seriously threatens human life and health. Drinking high-As groundwater for a long time will lead to various pathological changes such as skin cancer, liver cancer, and kidney cancer. High-As groundwater has become one of the most serious environmental geological problems in China and even internationally. This paper aims to systematically summarize the sources, migration, distribution, toxicological effects, and treatment techniques of As in natural groundwater in China based on a large number of literature surveys. High-As groundwater in China is mainly distributed in the inland basins in arid and semi-arid environments and the alluvial and lacustrine aquifers in river deltas in humid environments, which are in neutral to weakly alkaline and strongly reducing environments. The content of As in groundwater varies widely, and As(III) is the main form. The main mechanism of the formation of high-As groundwater in China is the reduced dissolution of Fe and Mn oxides under the action of organic matter and primary microorganisms, alkaline environment, intense evaporation and concentration, long-term water-rock interaction, and slow groundwater velocity, which promote the continuous migration and enrichment of As in groundwater. There are obvious differences in the toxicity of different forms of As. The toxic of As(III) is far more than As(V), which is considered to be more toxic than methyl arsenate (MMA) and dimethyl arsenate (DMA). Inorganic As entering the body is metabolized through a combination of methylation (detoxification) and reduction (activation) and catalyzed by a series of methyltransferases and reductases. At present, remediation methods for high-As groundwater mainly include ion exchange technology, membrane filtration technology, biological treatment technology, nanocomposite adsorption technology, electrochemical technology, and so on. All the above remediation methods still have certain limitations, and it is urgent to develop treatment materials and technical means with stronger As removal performance and sustainability. With the joint efforts of scientists and governments of various countries in the future, this worldwide problem of drinking-water As poisoning will be solved as soon as possible. This paper systematically summarizes and discusses the hot research results of natural high-As groundwater, which could provide a reference for the related research of high-As groundwater in China and even the world.

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## 1. Introduction

Arsenic (As) is a trace component in the crust, with an average concentration of 1.8 mg/kg (Rudnick RL et al., 2014), which is ubiquitous in nature. The most common As-rich

minerals are realgar (As<sub>2</sub>S<sub>2</sub>), pistillate (As<sub>2</sub>S<sub>3</sub>), As-pyrite (FeSAs), and As-sulfur-copper (Cu<sub>3</sub>AsS<sub>4</sub>) (Zhao Z et al., 2021). When As-bearing minerals are weathered, denudated, and leached, iron and manganese oxide minerals in aquifer sediments become the main carriers of As. Under hydrologic and biogeochemical processes, As in sediments will enter and occur in groundwater in the form of inorganic As(III) (arsenite) or As(V) (arsenate), continuously migrate and accumulate (Guo HM et al., 2019; Liu YC et al., 2021). High-As groundwater forms when As levels in groundwater exceed the drinking water standard set by the World Health

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Organization (WHO) by 10 µg/L.

At present, groundwater with high As content is distributed in more than 70 countries and regions around the world, mainly including India, Bangladesh, Cambodia, China, Vietnam, Myanmar, the United States, and other countries. The affected population reaches  $140 \times 10^6$  and shows an increasing trend (Smedley PL et al., 2002; Xu NZ et al., 2021) (Fig. 1). China is a typical area with high As content. Groundwater with high As content is distributed in 20 out of 34 provinces (Guo HM et al., 2019). This high-As groundwater has geographical characteristics and often occurs in alluvial lacustrine sedimentary aquifers in arid and semi-arid inland basins (such as the Hetao Basin, the Datong Basin, and the Guide Basin) and humid river deltas (such as the Jiangnan Plain) (Guo QH et al., 2015).

Groundwater, as the main source of drinking water, is the main way of human exposure to As. Most of the health problems related to As in the world are related to drinking groundwater with excessive As content. Long-term drinking of groundwater with high As content can cause various diseases, such as abnormal skin pigmentation, keratinization, conjunctivitis, lung cancer, skin cancer, visceral cancer, and other chronic As poisoning diseases. Even if one stops drinking groundwater with high As content, previous long-term ingestion of As can also cause irreversible or sustained adverse reactions (Narayan VM et al., 2018). Therefore, high As groundwater is a serious threat to human life and health, and it has become one of the most serious environmental geological problems facing China and even the world. It is urgent and important to systematically summarize the distribution and migration of high As groundwater, its toxicological effects, and remediation methods, and grasp its

future research trend.

Based on a large number of literatures, this paper systematically summarizes and discusses the latest achievements in the research of groundwater with high As content in recent years in China from five aspects: sources, migration, distribution, toxicological effects, and remediation methods. This review is conducive to researchers to understand the source, migration, and enrichment of As and its toxicological effects, helps researchers to better explore the practical feasibility of different As remediation methods, and finally provides a better reference for domestic and foreign researchers to carry out relevant research on primary groundwater with high As.

## 2. Sources of arsenic in groundwater

### 2.1. Natural sources

There are three main natural sources of As in groundwater: hydrothermal activities, ore deposits, and Cenozoic sediments (Deng YM et al., 2011; Scheiber L et al., 2016; Guo HM et al., 2019).

In active geothermal systems, As can be released in large quantities from As-rich minerals in deep reservoir rocks, and the content of As in geothermal water is generally high (Deng YM et al., 2011; Table 1). The intrusion of high-As geothermal water into surface aquifers can directly increase the concentration of As in groundwater (Guo QH et al., 2015), and the As in high-As geothermal water can be continuously adsorbed by surface riverbed or aquifer sediments (Nicolli HB et al., 2012).

Arsenic can be found in more than 200 different mineral

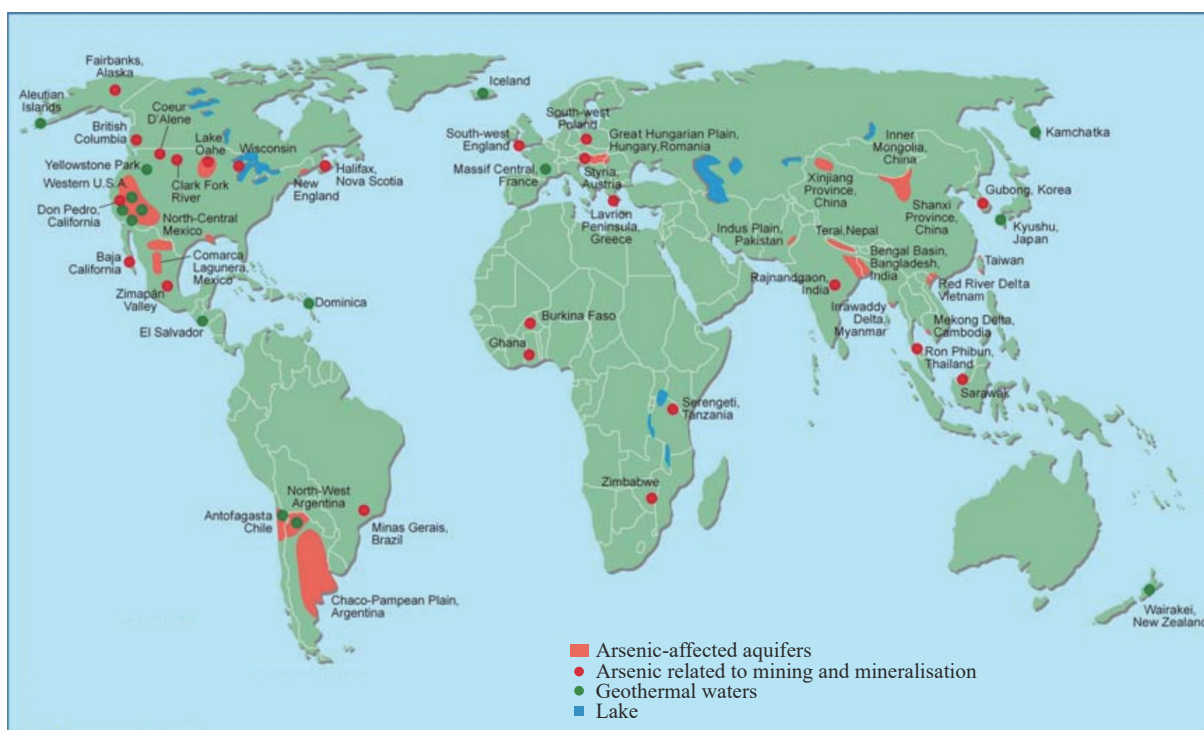


Fig. 1. Global distribution of high As groundwater (modified from Smedley PL et al., 2002).

forms in nature, of which 60% are arsenates, 20% are sulfides and sulfates, and the remaining 20% are arsenides, arsenates, oxides, and silicates (Zhao Z et al., 2021; Table 2). After As-bearing minerals in the As-rich rocks around the basin are weathered, denudated, and leached, the strong affinity of iron and manganese oxide minerals in the aquifer sediments makes them the most important new carriers of As, as well as the main source of As in the primary high-As groundwater (Guo HM et al., 2014). The results of stepwise extraction of As content in sediment samples from typical high-As groundwater distribution areas all show that the extractable As is positively correlated with the content of iron and manganese, and most As occurs in iron and manganese oxides in sediments (Guo HM et al., 2019; Zhang et al., 2022a).

## 2.2. Man-made Sources

Anthropogenic sources of As include agricultural activities such as coal burning, fertilizer, mining activities and pesticide application, and industrial activities such as mineral extraction and smelting (Scheiber L et al., 2016).

The content of As in coal samples (103–35000 mg/kg) collected in Guizhou Province is much higher than that in coal samples from Northeast, North, and East China (56–157 mg/kg) (He B et al., 2002). Arsenic in coal is mainly in the form of arsenite and arsenate. The main As-bearing minerals are pyrite and arsenopyrite (Ding ZH et al., 2001). Perennial burning of high-As coal in Guizhou Province and other areas leads to the concentration of As in the form of dust in the air up to 20–760 g/m<sup>3</sup>, and its residence time is about 7–10 days, and it settles to the surface after rainfall (Dai SF et al., 2005). According to statistics, there were about 3000 local patients with chronic arsenism caused by coal burning, such as skin lesions of hands and feet, trunk pigmentation, skin

keratinization, or skin cancer (Xie YX et al., 2001).

It is estimated that the total amount of As discharged by human activities into the atmosphere, water, and soil reached  $12 \times 10^6$ – $26 \times 10^6$  kg/a,  $12 \times 10^6$ – $70 \times 10^6$  kg/a, and  $52 \times 10^6$ – $112 \times 10^6$  kg/a, respectively (Sharma VK et al., 2009). During mining and smelting, As in As-bearing minerals is released, which can lead to a significant increase in As concentration in surrounding groundwater (Mukherjee A et al., 2014). Although the distribution of high-As groundwater around the ore body is generally localized, the tailings and sludge generated after the mining of the ore body extend the contamination to surrounding areas. After the chemical weathering of ore bodies excavated during mineral exploitation, sediments with high-As content are formed, which will become potential sources of As release (Orosun MM et al., 2021).

Arsenic is associated with other metallic minerals, such as copper, nickel, lead, and zinc. When these As-bearing minerals are mined or smelted, As will be released into the environment in large quantities, with an estimated annual discharge of 62000 t of As (Williams M, 2001). Arsenic concentrations in mine water range from 5 µg/L to 72 mg/L in seven countries in Southeast Asia, Africa, and Latin America (Smedley PL et al., 2002). In the early 1990s, a large-scale As poisoning incident occurred in Dali, Yunnan Province caused by non-ferrous metal smelting. Arsenic-containing dust discharged from the smelting plant made the concentration of As in the air several times exceed the standard, resulting in serious pollution of crops grown in this area (Xiao XY et al., 2008; Li B et al., 2013).

Sources of As in agricultural activities mainly include the use of As-bearing pesticides (such as insecticides and herbicides), the application of chemical fertilizers, and poultry feces, and sewage (Cai LM et al., 2015; Table 3). Arsenic

**Table 1. Content of As in different geothermal waters in the world.**

Country	Geothermal field	As/(µg/L)	Type of geothermal heat	Reference
China	Yangbajain	5700	Continental collision zone	Guo QH et al., 2015
America	Yellowstone National Park	1500	Magmation	Langner HW et al., 2001
Chile	Tatio	30000–40000	Magmation	Romero L et al., 2003
Russia	Kamchatka	2000–30000	Magmation	Ilggen AG et al., 2011
America	Salton Lake	30–12000	Invasion of granite	Alexander LF et al., 2017
Ecuador	Tambo River area	1090–7850	Magmation	Oyarzun R et al., 2004
Mexico	Los Humeros	500–162000	Magmation	Birkle P et al., 2010
New Zealand	Broadlands	5700–8900	Magmation	Simmons SF, 2000
Japan	Beppu Hot Spring	210–1360	Magmation	Takenaka T and Furuya S, 2008

**Table 2. Main As-bearing minerals in nature.**

Mineral	Chemical formula	Characteristic	Geologic origin
Arsenic ore	As	Light gray, nodular	Hydrothermal veins in crystalline rock
Orpiment	As <sub>2</sub> S <sub>3</sub>	Yellow to yellowish brown, resinous	Low-temperature hydrothermal mineralization and hot springs
Realgar	AsS	Red to orange, resinous prisms	A minor component of low-temperature hydrothermal mineralization and hot spring hydrothermal sulfide veins
Arsenopyrite	FeAsS	Silver to gray, metal prism, diamond cross-section	The most abundant As mineral forms at moderate to high temperatures
Scorodite	FeAsO <sub>4</sub> ·2H <sub>2</sub> O	Yellow-green to green-brown, Fibrous or granular	The principal minerals in hydrothermal sediments and secondary minerals in metallic ores

**Table 3. Main As-containing products in agricultural activities.**

Application	Ingredient	Chemical formula
Bactericide	Zinc methylarsonate	CH <sub>3</sub> -AsO <sub>3</sub> Zn
Insecticide	Calcium acid methylarsonate	CH <sub>3</sub> -AsO <sub>3</sub> Ca·H <sub>2</sub> O
Pesticide	Ferric methylarsonic amine	(CH <sub>3</sub> AsO <sub>3</sub> ) <sub>2</sub> FeNH <sub>4</sub>
Herbicide	Methyl sulfur arsene	CH <sub>3</sub> AsS
Bactericide	Urbacid	C <sub>7</sub> H <sub>15</sub> AsN <sub>2</sub> S <sub>4</sub>
Antiputrefactiva	Chromated copper arsenate	CuO·CrO <sub>3</sub> ·As <sub>2</sub> O <sub>3</sub>
Insecticide	Lead hydrogen arsenate	H <sub>3</sub> AsO <sub>4</sub> Pb
Insecticide	Monosodium methanearsenate	CH <sub>4</sub> AsNaO <sub>3</sub>
Bactericide	Methyl arsine oxide	CH <sub>3</sub> AsO
Pigment	Copper arsenite acetate	Cu(CH <sub>3</sub> COO) <sub>2</sub> ·3Cu(AsO <sub>2</sub> ) <sub>2</sub>

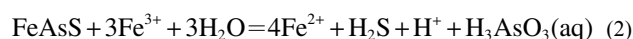
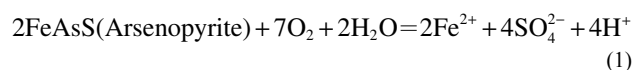
residues can be as high as 2 g/kg in soils with long-term use of arsenide, herbicide, and insecticide, and as high as 0.22 g/kg in soils near a company that produces wood preservative salts (Sadler R et al., 1994). Sources of As from industrial activities include wood preservatives (chromified copper arsenate), As-bearing paint (As trioxide), electronic waste, corrosion-resistant materials, industrial wastewater, etc. (Bhattacharya P et al., 2007).

### 3. Main enrichment mechanism of arsenic in groundwater

#### 3.1. Oxidation of arsenic-rich sulfide minerals

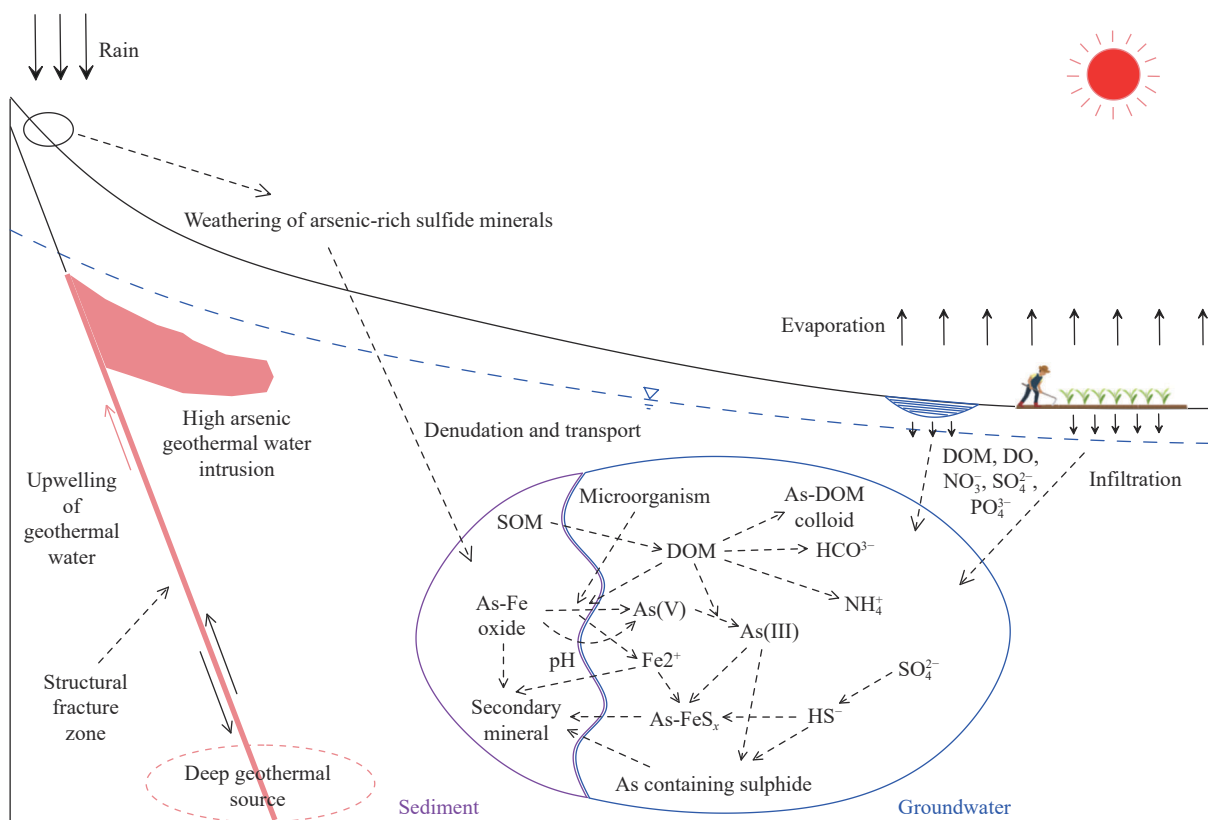
Arsenic-rich sulfide minerals in mineralized zones (such

as pyrite, arsenopyrite, erythematous, and realgar) will be oxidized after contact with the atmosphere (Equations 1 and 2), resulting in the release of As in their crystal lattices and leaching into groundwater by rainfall to increase As concentration (Dong YH et al., 2018; Fig. 2). However, large amounts of iron and manganese oxides occur in aquifer sediments, which can adsorb As from groundwater and thus reduce As concentrations in groundwater (Anawar HM et al., 2004). The formation of high-As groundwater depends on the difference between As released by As-rich minerals and As adsorbed by iron and manganese oxides and groundwater circulation conditions.



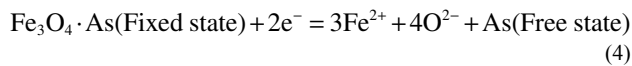
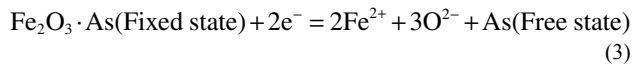
#### 3.2. Reductive dissolution of arsenic-containing iron-manganese oxides

Degradation of organic matter in groundwater systems drives a series of complex REDOX reactions in aquifers, in which the reducing dissolution of As-bearing Fe and Mn oxides lead to the release of As into groundwater in large quantities (Equations 3 and 4) (Lawson M et al., 2016; Shi WJ et al., 2021) (Fig. 2). In addition, dissolved As(V) in groundwater and adsorbed As(V) on sediments can be dissimilated to As(III) with stronger activity, thus promoting



**Fig. 2.** Key processes of arsenic migration in natural groundwater systems.

As enrichment in groundwater (Guo HM et al., 2013). Under strong reduction environment conditions, some  $\text{SO}_4^{2-}$  in groundwater will undergo a reduction reaction, and the reduction product  $\text{S}^{2-}$  will further affect the circulation of As and Fe in groundwater (Gao ZP et al., 2021). During the transformation of different types of iron oxide minerals in sediments, mineral structure (volume and surface area) and REDOX state will be changed, thus affecting the binding ability of minerals with As (Liu LH et al., 2021).



Dissolved organic matter in groundwater can also provide a carbon source for microbial metabolic activities and catalyze and accelerate the biogeochemical process of As in groundwater systems. The reducing dissolution of iron and manganese oxides in aquifers is the result of the joint action of organic matter and microorganisms (Xie XJ et al., 2015). Microorganisms such as iron-reducing bacteria, As-reducing bacteria, and sulfur-reducing bacteria have been isolated from high-As aquifers. Laboratory experiments have demonstrated that biogeochemistry with the participation of microorganisms plays a very important role in As transport and accumulation (Qiao JT et al., 2017; Xie ZM et al., 2018).

### 3.3. Desorption of arsenic in the alkaline environment

The adsorption capacity of iron and manganese oxide minerals to As decreases with the increase of pH, so the As adsorbed on mineral surface is easy to be desorbed to groundwater under alkaline conditions (You YJ et al., 2019). In addition, a rise in pH increases the density of negative charges on the surfaces of colloids and clay minerals, thus facilitating the release of adsorbate As into groundwater (Dixit S et al., 2003; Fig. 2). Increase in pH value will cause the desorption of other ions on the mineral surface (such as phosphoric acid and bicarbonate, etc.). Phosphoric acid and bicarbonate in groundwater can compete with the oxygen-containing anions of As for the adsorption sites on the sediment surface (Guo QH et al., 2015), resulting in the release of part of As originally adsorbed on the mineral surface into the water (Bhattacharya P et al., 2007; Kanematsu M et al., 2013).

### 3.4. Influence of geothermal activity

Geothermal water is generally characterized by high As and high temperature. The high-As geothermal water has been found in many countries around the world. For example, the content of As in the geothermal field of the Rioloa Basin in Chile is 27.0 mg/L (Romero L et al., 2003). The content of As in the geothermal field in Honshu, Japan is 13.0 mg/L (Pascua CS et al., 2007), and the content of As in the Yangbajing geothermal field in Tibet is about 5.7 mg/L (Guo Q et al., 2007).

When geothermal water with high-As content intrudes into aquifers or is exposed on the surface, the concentration of As in groundwater around the ground will increase significantly (Deng YM et al., 2011). The groundwater with high-As content caused by the intrusion of geothermal water into aquifers has been discovered successively in the Qinghai-Tibet Plateau (Zhang YF et al., 2017). High-As geothermal water can continuously invade aquifers through fault zones, resulting in As migration and enrichment in groundwater to form high-As groundwater (Fig. 2). Temperature, pH, Eh, mineral phase and mixing ratio in aquifers in geothermal areas are key factors to control As content in groundwater (Jiang J et al., 2008).

The heat conduction effect of geothermal sources on the overlying aquifer will increase the temperature of the aquifer, accelerate the degradation of organic matter in aquifers, promote the reducing dissolution of iron and manganese oxide minerals, and thus lead to more As being released into the groundwater (Matthijs B et al., 2013). At the same time, as As adsorbed on the surface of sediments is an exothermic reaction (Table 4), rising temperatures will promote the desorption of As in the adsorbed state on the surface of sediments into groundwater (Sun ZX et al., 2006). Therefore, geothermal activity may affect the release and migration of As in aquifers through direct invasion or indirect heat conduction.

### 3.5. Impacts of human activities

The global groundwater with high-As content is mainly of geological origin, but human activities can also affect the variation of As content in groundwater. Untreated As-bearing wastewater is discharged directly into surface water in industrial production, which will increase As concentration in groundwater after intrusion into aquifers (Liao TQ et al., 2020). Irrigation activities for large-scale groundwater exploitation can affect the groundwater flow field inside and between adjacent aquifers, increase the hydraulic gradient

**Table 4.** Reaction enthalpy of As adsorption process.

Materials	Temperature/°C	$\Delta H/(\text{kJ/mol})$	Reference
Natural sediment	5, 11, 25, 60	-56.4–-84.0	Matthijs B et al., 2013
Iron-containing waste (mainly iron-containing oxides)	20, 25, 30	-161.8	Negrea A et al., 2010
Bauxite (mainly containing iron and aluminum oxides)	25, 35, 45	-109.5	Maji SK et al., 2007
Zero-valent iron	25, 35, 45	-112.41–-11.9	Kanel SR et al., 2005
Goethite	25, 35, 45	-27.6–-26.0	Kersten M et al., 2009
Iron-aluminum binary mixed oxide	10, 25, 50, 60	-12.64	Hong HJ et al., 2011

between aquifers of different depths, and increase the intensity of groundwater recharge by infiltration of surface water such as ponds and rivers (Polizzotto ML et al., 2013). Harvey CF et al. (2006) found that large-scale irrigation activities of groundwater exploitation in Bangladesh caused great fluctuation of groundwater level, resulting in more infiltration of surface water bodies such as ponds and rivers to recharge groundwater, and a large amount of dissolved organic matter then entered aquifers, which eventually lead to a large amount of As in sediments being released into the groundwater, contributing to the formation of high-As groundwater in Bangladesh. The entry of large amounts of dissolved organic matter in surface water bodies into aquifers will lead to changes in related hydrological and biogeochemical conditions (McArthur JM et al., 2016), which may result in the oxidation of sulfide minerals in the sediment or the reducing dissolution of As-bearing iron and manganese oxide minerals, thus releasing more As into the groundwater and forming groundwater with high-As content (Harvey CF et al., 2006; Kumar S et al., 2021; Fig. 2). In addition, active organic matter invading groundwater can promote the release and migration process of As in aquifers by stimulating microbial metabolic activities (Kim K et al., 2009; Guo HM et al., 2012). Polizzotto ML et al. (2008) found that the main source of As in groundwater in the Mekong region of Cambodia was the wetland sediments covering the surface. A large number of active organic matter infiltrated into the aquifer along with the river water, which promoted microbial activities, thus leading to the reduced dissolution of a large

number of iron oxide minerals in the sediments. The fixed As was released into groundwater, resulting in abnormal As concentration in groundwater.

Therefore, anthropogenic activities can affect the hydrologic and biogeochemical processes in aquifers through the input of exogenous substances or interference with water flow paths, thus affecting the release and migration of As in aquifers.

#### 4. Distribution areas of typical high-arsenic groundwater in China

Groundwater in China with high-As content is mainly distributed in inland basins under arid and semi-arid environments and reductive aquifers of alluvial and lacustrine facies in river deltas under humid environment, such as the Hetao Basin (Guo HM et al., 2019), the Datong Basin (Xie XJ et al., 2009), Guide Basin (Wang Z et al., 2018) and Jiangnan Plain (Li JX et al., 2013). Domestic and foreign researchers have carried out extensive and in-depth studies focusing on the high-As groundwater in these areas (Fig. 3).

##### 4.1. The Hetao Basin

The Hetao Basin is one of the representative areas of endemic As poisoning in China. Groundwater with high-As content is widely distributed in the basin, and the life and health of more than  $1 \times 10^6$  local residents are seriously threatened (Guo HM et al., 2008). The Hetao Basin is located in the west of Inner Mongolia, and the terrain is high in the

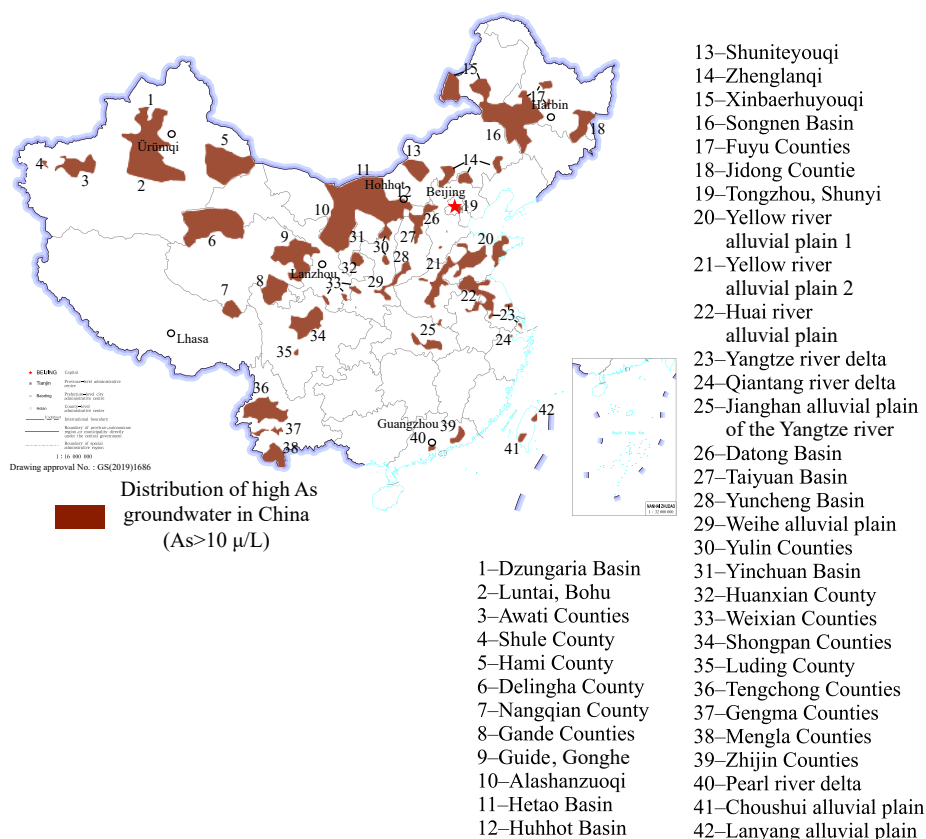


Fig. 3. High-arsenic groundwater distribution map in China (modified from Guo HM et al., 2014).

southwest and low in the northeast. It has an arid and semi-arid climate. The annual average precipitation is about 188 mm, the annual evaporation is 2000–2500 mm, and the annual average temperature is 5.6°C–7.8°C. The thickness of the fine clastic sediments of the Quaternary lacustrine facies in the basin is between 200 m and 1500 m. With the frequent reroute of the Yellow River, a large number of residual lakes and oxbow lakes were formed, and thick humus and silt layers rich in organic carbon (0.44%–5.57%) were deposited inside the basin (Gao CR et al., 2010).

Groundwater in the Hetao Basin is in a neutral to weakly alkaline (pH 7.35–8.80) and strongly reducing environment, with high Fe (66.1–7075 µg/L) and EC (0.79–7.00 mS/cm) values (Jia YF et al., 2017). Groundwater with high-As content mainly occurs in shallow alluvial lacustrine aquifers composed of black or dark gray fine sand, with As content ranging from 3.38 µg/L to 936 µg/L (Table 5), and inorganic As(III) accounts for about 75% of the total As (Guo HM et al., 2014; Zhang Z et al., 2020). The average content of As in the sediments of alluvial fans and aquifers in the plain of the Hetao Basin is 18.9 mg/kg (7.3–73.3 mg/kg). The initial source of As in sediments is As-rich sulfide minerals and biotite in the bedrock of Langshan Mountain in the north of the basin (Guo HM et al., 2015; Zhang Z et al., 2022b).

The formation mechanism of high-As groundwater in the Hetao Basin is mainly due to the reductive dissolution of iron and manganese oxides under the action of organic matter and microorganisms, which lead to the release of As adsorbed on mineral surfaces into groundwater and the dissimilar reduction of the accompanying As(V) into more active As(III), which continuously migrates and accumulates in groundwater (Guo HM et al., 2019). The nitrogen cycle in aquifers affects the release and migration of As in aquifers by regulating the conversion between Fe(III) oxides and dissolved Fe(II). For example, the mineralization of organic matter (including organic nitrogen) promotes the reducing

dissolution of Fe(III) oxides, releasing Fe(II) and As into groundwater (Gao ZP et al., 2021). In addition, the Hetao Basin is one of the earliest and largest irrigation areas of the Yellow River in northern China. Strong evapotranspiration leads to seasonal accumulation of salt in the soil. About half of the soil in the basin contains salt and alkali. Salinization is conducive to the release of As from aquifers to some extent (Jia YF et al., 2017). Fine-grained organic colloids in groundwater can bind to As, thus affecting the migration and distribution of As in groundwater (Guo HM et al., 2009). HCO<sub>3</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup> in groundwater compete with As for binding sites on the surface of iron and manganese oxides, leading to a partial release of adsorbed As into groundwater (Gao ZP et al., 2020). In addition, some studies believe that mining activities in front of Langshan Mountain in the northern part of the basin resulted in a large amount of As from As-rich minerals being released into groundwater (Deng YM et al., 2011).

#### 4.2. The Datong Basin

The Datong Basin is located in the semi-arid region of northern China, belonging to one of the Cenozoic faulted basins. The basin is distributed in a strip from northeast to southwest, with mountains in the southeast and northwest, and broad and flat in the middle. The Sanggan River and Huangshui River traverse the basin from southwest to northeast, and the thickness of Quaternary sediments increases from 200 m at the edge of the basin to 2700 m in the middle of the basin. The climate of the Datong Basin is mainly arid with little rainfall and high wind and sand. The average annual temperature, rainfall, and evaporation are 6.5°C, 225–400 mm, and 2000–2155 mm, respectively (Xie XJ et al., 2009).

In the Datong Basin, high-As groundwater mainly occurs in alluvial and lacustrine aquifers at depths ranging from 15 m to 60 m, with As concentrations up to 330 µg/L (Table 6). As(III) accounts for 55%–66% of total As in groundwater, with pH values ranging from 7.0 to 8.8 (Li JX et al., 2013; Xie XJ et al., 2015). The most important source of As in aquifers in the Datong Basin is the coal-bearing strata of Carboniferous-Permian outcropping in the western part of the basin, in which As content (average 103 mg/kg) is relatively higher than that in other rock types (0.4–4 mg/kg) (Xie XJ et

**Table 5. Statistical table of groundwater chemical composition in the Hetao Basin (Data from Guo HM et al., 2014; Zhang Z et al., 2020).**

Parameter	Unit	Number of water samples (n=42)			
		Min	Max	Average	Median
Temperature	°C	9.97	26.8	14.7	13.5
pH	–	7.35	8.80	7.94	7.85
EC	mS/cm	0.79	7.00	3.33	3.94
As	µg/L	3.38	936	229	112
Fe	µg/L	66.1	7075	1412	831
Mn	µg/L	3.6	1162	303	171
Cl <sup>-</sup>	mg/L	45.8	1109	454	483
NO <sub>3</sub> <sup>-</sup>	mg/L	–	30.9	2.43	–
HCO <sub>3</sub> <sup>-</sup>	mg/L	180	1018	663	704
SO <sub>4</sub> <sup>2-</sup>	mg/L	–	1018	235	128
Ca <sup>2+</sup>	mg/L	9.15	181	71.5	53.3
Mg <sup>2+</sup>	mg/L	15.4	192	80.9	69.5
Na <sup>+</sup>	mg/L	74.1	939	431	465
K <sup>+</sup>	mg/L	2.31	8.08	5.15	5.39

**Table 6. Statistical table of groundwater chemical composition in the Datong Basin (Data from Han Y et al., 2017).**

Parameter	Unit	Numbers of samples	Min	Max	Average
As	µg/L	141	0.2	303	27.7
F	mg/L	141	0.17	4.21	0.96
I	mg/L	141	0.002	1.23	0.07
pH	–	141	7.0	8.8	7.9
TDS	mg/L	140	354	6582	1045
NH <sub>4</sub> <sup>+</sup>	mg/L	140	0.25	1.81	0.17
NO <sub>3</sub> <sup>-</sup>	mg/L	141	0.05	46	8.26
NO <sub>2</sub> <sup>-</sup>	mg/L	141	0.0009	0.98	0.20

al., 2015). The organic lake sediments in the basin is secondary As-rich medium (0.3–44 mg/kg). The high-As groundwater distribution area in the Datong Basin is characterized by strong evaporation, active water-rock interaction, thick lacustrine sedimentary layer, low groundwater flow rate, and weak alkaline environment (Pi KF et al., 2017).

Degradation of organic matter in aquifers drives the reduced dissolution of Fe and Mn oxides leading to the release of As from aquifer sediments into groundwater (Yu Q et al., 2015). An alkaline environment is conducive to the desorption of As from the surface of oxide minerals, increasing the concentration of As in groundwater (Wang YX et al., 2009). Strong evaporation and concentration, long-term water-rock interaction, and slow groundwater flow rate lead to continuous migration and enrichment of As in groundwater (He XD et al., 2020). Large-scale farmland irrigation causes REDOX active components such as dissolved organic matter, O<sub>2</sub>, and NO<sub>3</sub><sup>-</sup> to enter aquifers, affecting the release and migration of As in shallow aquifers (Xie XJ et al., 2015). Harvey CF et al. (2006) found that the irrigation activities of large-scale groundwater exploitation by local people lead to the infiltration of more surface water such as ponds and rivers to recharge the groundwater, and a large number of dissolved organic matter then entered the aquifer, resulting in a large amount of As in the sediments being released into the groundwater, resulting in abnormal As concentration in the groundwater. In addition, Kim K et al. (2009) found that the irrigation of farmland with good recharge conditions would bring a large number of surface oxidants such as sulfate or nitrate into groundwater, which enhanced groundwater oxidation and thus reduced the As concentration.

#### 4.3. The Guide Basin

The Guide Basin is located in the eastern part of Qinghai Province, the transition zone between the Loess Plateau and the Qinghai-Tibet Plateau. The whole area is crisscrossed with ravines, alternating between mountains and rivers. The water system is developed, presenting multilevel river terraces and hilly landforms. The plateau has a continental climate with long illumination times, strong solar radiation, and a large diurnal temperature difference. The average annual temperature is 7.2°C, the annual rainfall is about 300 mm, and the evaporation is as high as 1400 mm (Liao Y et al., 2013). There are abundant geothermal resources at the bottom of the Guide Basin, and the thermal energy of the basement hot rock mass is continuously transmitted upward through thermal controlled faults and spreads laterally along the strata to form layered heat reservoirs. The temperature gradient in the inland basin (average 7.9°C/100 m) is much higher than the global average geothermal gradient (3°C/100 m) (Tang XC et al., 2020).

Groundwater with high-As content occurs in deep confined aquifers in the Guide Basin, with the highest concentration reaching 355 µg/L (Wang Z et al., 2018; Table 7). More than 59000 local people are threatened by water-borne As poisoning due to long-term drinking of groundwater with

**Table 7. Hydrochemical parameters of confined groundwater in the Guide Basin, Qinghai Province.**

Parameter	Unit	Number of water samples (n=20)			
		Min	Max	Average	Median
As	µg/L	9.87	377	108	68.5
ORP	mV	-175	-9.5	-81.0	-77.0
pH	-	8.38	9.08	8.79	8.81
Temperature	°C	13.7	25.2	19.4	19.5
TDS	mg/L	290	730	475	487
NH <sub>4</sub> <sup>+</sup> -N	mg/L	0.01	0.59	0.19	0.25
TOC	mg/L	0.42	2.14	0.96	0.76
Fe	µg/L	6.12	129	31.2	22.5
Mn	µg/L	2.93	26.3	6.99	4.68
Ca <sup>2+</sup>	mg/L	3.05	14.3	7.10	7.66
K <sup>+</sup>	mg/L	0.99	3.14	1.61	1.51
Mg <sup>2+</sup>	mg/L	0.07	5.08	0.90	0.37
Na <sup>+</sup>	mg/L	91.9	280	173	175
Cl <sup>-</sup>	mg/L	35.6	230	116	108
NO <sub>3</sub> <sup>-</sup>	mg/L	bdl	0.84	0.35	0.34
HCO <sub>3</sub> <sup>-</sup>	mg/L	92.7	388	197	168
SO <sub>4</sub> <sup>2-</sup>	mg/L	60.6	145	98.7	91.2

Note: “bdl” is short for “below detectable limit”

high-As content (Lang XJ et al., 2016). Iron and manganese oxide minerals in sediments of the Guide Basin are the main carriers of As and the main sources of As in groundwater with high-As content in the basin. The groundwater with high-As content in the Guide Basin has a higher pH value (8.38–9.08) and water temperature (average 19.4°C), and lower concentrations of Fe (6.12–129 µg/L), Mn (2.93–26.3 µg/L) and TOC (0.42–2.14 mg/L) than the groundwater with high-As content in other areas.

The main mechanism of As migration and enrichment in groundwater of confined aquifers in the Guide Basin is the reductive dissolution of As-bearing iron oxides under reducing conditions and the desorption of As from the sediment surface under an alkaline environment (Wang Z et al., 2018). The weathering of silicate minerals in confined aquifers is another important process for the formation of high-As groundwater in the Guide Basin, and the rise of groundwater temperature is conducive to silicate weathering and As migration and enrichment in groundwater (Xing SP et al., 2022). Release of As from sediments is facilitated by electron shuttling, complexation, and competitive adsorption of refractory organic molecules in groundwater (i.e., polycyclic aromatic hydrocarbons and polyphenols), which are influenced by water temperature and pH (Qiao W et al., 2021). In addition, the alkaline environment and closed hydrogeological conditions of confined aquifers facilitate the continuous migration and accumulation of As along the flow path, resulting in the formation of high-As groundwater in the central basin (Wang Z et al., 2018).

#### 4.4. The Jiangnan Plain

The Jiangnan Plain is an alluvial plain formed by the

Yangtze River and its largest tributary Han River. It is a typical river delta area with high As distribution in groundwater in southern China and has become a hot spot in the study of high-As groundwater in recent years.

The Jiangnan Plain is a subtropical monsoon climate, the annual temperature is between 15°C and 17°C, and annual average precipitation and evaporation are about 1200 mm and 1378 mm, respectively. The depth of groundwater is shallow. Hydraulic connection is close between surface water and groundwater. Compared with inland arid basins, groundwater in the Jiangnan Plain is dominated by HCO<sub>3</sub>-Ca·Mg type with low TDS, but aquifers are rich in organic matter, forming a strongly reducing environment (Jia YF et al., 2018). Groundwater with high-As content mainly occurs in shallow aquifers with depths ranging from 10 m to 45 m, and the content of As in groundwater ranges from 0.57 µg/L to 2320 µg/L, with an average of 217 µg/L (Table 8). The content of As (11–108 mg/kg) in sediments of the Jiangnan Plain is higher than that in sediments of the above-mentioned basins (Xie ZM et al., 2018).

Indigenous microorganisms in the aquifer of the Jiangnan Plain affects the dynamic balance of As in the aquifer by controlling the As adsorption/desorption and REDOX environment (Stuckey JW et al., 2016). The combined action of organic carbon in aquifers and *in situ* microorganisms (such as Clostridiaceae) promotes the reducing dissolution of As-bearing iron and manganese oxides, resulting in the release of As from sediments into groundwater (Besold J et al., 2019; Sun Y et al., 2021). The spatial distribution of As in groundwater is controlled by the form of As in sediments, while the seasonal variation of As concentration and form in groundwater affects the content and form of As in sediments

**Table 8. Hydrochemical parameters of groundwater in the Jiangnan Plain of southern China (Data from Xie ZM et al., 2018).**

Parameter	Unit	Number of water samples (n=34)			
		Min	Max	Average	Median
As	µg/L	0.57	2320	217	67.9
pH	–	6.56	7.51	7.08	7.10
Fe	mg/L	0.02	13.0	5.23	4.17
Mn	mg/L	0.07	11.4	1.62	0.87
Cl <sup>-</sup>	mg/L	0.46	71.7	10.4	4.48
SO <sub>4</sub> <sup>2-</sup>	mg/L	0.01	101	5.87	0.07
NO <sub>3</sub> <sup>-</sup>	mg/L	0.01	7.71	1.34	0.22
HCO <sub>3</sub> <sup>-</sup>	mg/L	415	799	559	532

(Duan YH et al., 2017). Microorganisms and exogenous substances (such as As phosphorus, organic carbon, humus, phosphate, and small molecular organic acids) have also been implicated in the release of As from aquifers (Dai XY et al., 2018). The seasonal variation of As concentration in groundwater in the Jiangnan Plain is related to the biodegradation of active organic matter, while the terrestrial high molecular weight humus affects the seasonal variation of As concentration in groundwater through complexing reaction (Yang YJ et al., 2020).

## 5. Toxicological effects of arsenic in groundwater

### 5.1. Toxicity of arsenic

Arsenic is a toxic and carcinogenic chemical (Narayan VM et al., 2018). The term As-poisoning was first proposed by Mazumder DNG et al. (1988) and was later used by the World Health Organization (WHO) to describe the effects of chronic As-poisoning on human health (IARC, 2004). Worldwide, millions of people are continuously ingesting excessive As through drinking contaminated water or eating food irrigated and grown with contaminated water (Rahman A et al., 2018).

Arsenic has unique physical and chemical properties and can cause acute or chronic poisoning (An Y et al., 2015; Bhattacharjee P et al., 2013). The symptoms of acute As poisoning are vomiting, muscle cramps, abdominal cramps, and tingling in the hands and feet (Sinha D et al., 2020). Chronic symptoms caused by long-term exposure to As are not specific (e.g. weight loss, chronic weakness), and its chronic toxicity can adversely affect the entire multi-organ system, i.e. Arsenic can affect the whole body in some way (Table 9; Rahman A et al., 2018). Arsenic is beneficial to the human body in small amounts and can boost human metabolism, but long-term ingestion of excessive As can have non-carcinogenic and carcinogenic effects on the human body. Non-carcinogenic effects of As include respiratory disease, gastrointestinal dysfunction, liver disease, cardiovascular disease, neurotoxicity, diabetes, miscarriage, and infant death (Edmunds WM et al., 2015). Carcinogenic effects of As include squamous cell carcinoma, Baud's disease, basal cell carcinoma, bladder cancer, lung cancer, liver cancer, and kidney cancer (Mochizuki H et al., 2019). The body can transform or mitigate the toxic accumulation of As through methylation and urine excretion, but the detoxification process is individualized and influenced by

**Table 9. Chronic diseases potentially caused by long-term ingestion of arsenic.**

Organ	Disease	References
Skin	Keratosis, melanosis, Bowen's disease, squamous cell carcinoma	Kuo YC et al., 2017
Lungs and throat	Lung function injury, shortness of breath, lung cancer, laryngeal cancer	Ahmed S et al., 2017
Blood vessels and heart	Peripheral vascular disease, hypertension	Edmunds WM et al. 2015
Kidney and bladder	Kidney cancer, bladder cancer	Goswami R et al. 2020
Nerves and brain	Neuropathy and headache	Hong YS et al., 2014
Pancreas	Diabetes	Edmunds WM et al., 2015
Prostate and uterus	Prostate cancer and miscarriage	Roh T et al., 2018

genetic and environmental factors (Smith AH et al., 2018).

Arsenic exists in organisms in different concentrations and chemical forms, and the toxicity of different forms of As is obviously different. The toxicity of As(III) is much higher than that of As(V) because As(III) can interfere with the reaction process of some enzymes (such as pyruvate dehydrogenase) by binding to sulfhydryl (-SH) or hydroxyl (-OH) functional groups (Kligerman AD et al., 2007). As(V) can replace phosphate in the synthesis of adenosine triphosphate (ATP) and inhibit the energy metabolism process of cells (Zhang HY et al., 2016). As(III) and As(V) are thought to be more toxic than MMA and DMA, and trivalent methyl arsenide is more acute and genotoxic than pentavalent methyl arsenide (Souza ACM et al., 2019). Arsenic has also been shown to be a genotoxin capable of mutational effects at the DNA sequence level, inducing the formation of chromosomal aberrations (CA), sister chromatid exchange (SCE), and micronucleation (MN) in mammalian cells (Das N et al., 2016; Zhang W et al., 2021).

## 5.2. Arsenic metabolism

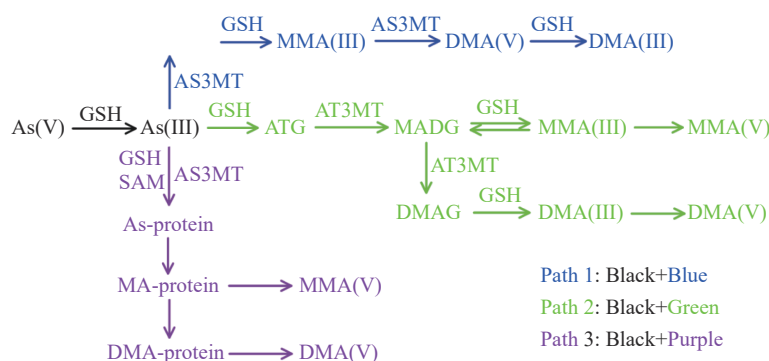
Arsenic ingested by humans is absorbed in the digestive tract and transported to body tissues through the blood (Ferrario D et al., 2009). Arsenic in the blood binds to oxygenated hemoglobin, resulting in extensive destruction of red blood cells, reducing blood's ability to deliver oxygen to vital organs, and affecting the normal functioning of the kidneys and liver (Kan R et al., 2022). Small amounts of As can be preferentially bound to proteins such as keratin and retained in tissues such as hair and nails (Slotnick MJ et al., 2006). Most of the ingested As enters the liver for methylation metabolism, and the newly formed As metabolites are less reactive with the internal tissues, and most of them are finally excreted in the urine (Cohen SM et al., 2006; Brauner EV et al., 2014). Arsenite binds to the protein sulfhydryl (-SH) in various tissues in the human body, including the lungs, spleen, liver, kidney, and gastrointestinal mucosa (Raml R et al., 2005). Arsenic betaine and As sugar are non-toxic forms of As. Generally, As betaine will not change after ingestion, but As sugar can be metabolized into various As-bearing compounds (Zhang Y et al., 2019).

Inorganic As entering the human body is metabolized through a combination of methylation (detoxification) and reduction (activation), catalyzed by a series of methyltransferases and reductases, respectively (Pei J et al., 2018). There are three conceptual models available to describe the processes of As metabolism and methylation (Fig. 4). In the first type of As metabolism, inorganic As is converted to methyl As by alternating reduction and oxidation of methyl groups (Thomas DJ, 2007; Bhowmick S et al., 2017). The reduction process uses glutathione (GSH) as the electron donor and is catalyzed by As(V) reductase. The oxidation and methylation process uses active adenosine methionine (SAM) as the methyl donor and is catalyzed by As(III) methyltransferase (AS3MT) (Zhang JY et al., 2016). In the second As metabolism process, it is assumed that As metabolism is carried out through the As-glutathione complex, where trivalent methyl As is the predecessor of its pentavalent form (Hayakawa T et al., 2005). A third metabolic pathway for As assumes that in the presence of glutathione and active adenosine methionine (SAM), As can bind to both soluble and insoluble proteins and then undergo a continuous reduction methylation process of AS3MT (Naranmandura H et al., 2006).

Most of the As ingested by humans is methylated and excreted as DMA (79%–85%), with small amounts as inorganic As (8%–16%) or MMA (5%–6%) (Scholz C et al., 2005). Arsenic methylation is thought to be a detoxification mechanism, and assessing the various metabolites involved in the excretion of As could provide new insights into the complex relationship between As metabolism and toxicity. Tests of human urinary As metabolites were used to correlate As exposure with As intake, mechanisms of As methylation, human bioaccumulation, and excretion capacity, and to identify carcinogenic or non-carcinogenic health effects (Rivera-Nunez Z et al., 2011).

## 6. Remediation technologies

High concentration of As in groundwater threatens the life and health of millions of people all over the world. Therefore, it is urgent to explore economic, ecological, efficient, and recyclable means of groundwater restoration with As. After



**Fig. 4.** Metabolic pathway of arsenic (modified from Bhowmick S et al., 2017). MMA—methyl arsenate; DMA—dimethyl hypoarsenic acid; GSH—glutathione; AS3MT—As(III) methyltransferase; ATG—As triglutathione; MADG—monomethyl As diglutathione; DMAG—dimethyl As glutathione; SAM—active adenosine methionine; MA—monomethyl As; DMA—dimethyl As.

decades of joint efforts by many governments and scientists around the world, the remediation technology of high-As groundwater has made considerable progress (Table 10), which is mainly reflected in the following aspects.

### 6.1. Ion exchange

An ion exchange system is a technology that can effectively remove As from water. The synthetic resin in the ion-exchange system can stably absorb metal-like ions, allowing the ions to exchange between the solid resin phase and solution phase (Sarkar A et al., 2016). Chen ASC et al. (2020) showed that As in drinking water could be effectively

removed through ion exchange coupled with strong base anion resin. However, the efficiency of ion-exchange technology is affected by several factors, including the coexistence of contaminants, As concentration, pH, and resin type (Cao WG et al. 2022). Further research is needed to determine the most appropriate resin types and parameters for this technology.

### 6.2. Membrane filtration

Pores in the membrane allow certain components of the mixture to pass through while retaining others, thus acting as a selective barrier, and a membrane filtration process can be

**Table 10. Different remediation methods for high arsenic water.**

Method	Technology	Mechanism	Removal efficiency	Advantage	Disadvantage	References
Physics	Ion exchange	Use a synthetic resin bed	95%	It is not affected by pH and is affected by many other factors	Only effective for arsenite removal; needs to be replaced	Chen ASC et al., 2020
Physics/Chemistry membrane filter procedure	Ultrafiltration and microfiltration	Ion separation driven by low pressure	Low concentration 95%; High concentration 40–65%	Easy to operate; low energy consumption; low cost	As removal efficiency is low	Wan P et al., 2020
	Nanofiltration	High-pressure separation of ions	>95%	As(V) removal efficiency is high	Material corrosion needs to be controlled; pre-oxidation of As(III) is required	Schmidt SA et al., 2016
	Reverse osmosis membrane	High-pressure separation of ions	86%–99%	As(V) removal efficiency is high; safety handling; simple Maintenance	High investment costs; material corrosion needs to be controlled	Schmidt SA et al., 2016
Biotreatment	Sphingofilament algae	Accumulation and tolerance of cells to As	>95%	Cyanobacteria are widely distributed in freshwater ecosystems	Genes involved in As biotransformation are still unknown	Zhu F et al., 2020
	Nostoc	Intracellular uptake of As	90%	Ubiquitous in freshwater ecosystems; a variety of As bioconversion pathways; can survive high concentrations of As	Bioaccumulation of As in cyanobacteria biomass may affect its use in wastewater treatment	Xue XM et al., 2017
	Mosses Candida	Intracellular accumulation of As(III) and As(V)	90%	Accumulation of As can be promoted through nutritional supplements	Lack of studies using the strain; bioaccumulation of As in biomass risk of As entering the food chain	Cao WG et al., 2022
	microcystis aeruginosa	Removal and bioremediation of As from water	95%	Efficient uptake of As(V); conversion and methylation of As to a less toxic form	Further research is needed on the long-term effects of As on species	Wang Y et al., 2015
Nano-particles	ZIF-8 nanoparticles	Adsorption of As(III) and As(V)	>97%	High stability in water; High thermal and mechanical stability	Subjectively, the mechanical understanding of ultrastructural morphology is still lacking	Jian M et al., 2015
	Copper oxide nanoparticles	Adsorption of As in water	88.4%–97.8%	As(III) removal efficiency is high	High material cost	Kumar I et al., 2020
Electrochemistry	Electrochemistry	Many forms of iron (hydrogen) oxides are produced to adsorb and oxidize As in water	>90%	High removal efficiency of As; No pollution; The removal of As(III) does not require a pre-oxidation process	High energy consumption; Maintain the electrodes regularly	Rathi BS et al., 2021

used to remove As from water. At present, membrane filtration processes mainly include microfiltration (membrane diameter 0.1–10  $\mu\text{m}$ ), ultrafiltration (membrane diameter 0.01–0.10  $\mu\text{m}$ ), nanofiltration (membrane diameter 0.10–0.01  $\mu\text{m}$ ) and reverse osmosis (membrane diameter 0.0001  $\mu\text{m}$ ) (Choong TSY et al., 2007; Sarkar A et al., 2016). Microfiltration and ultrafiltration are low-pressure driven separation techniques commonly used to remove organic matter, suspended particles, macromolecules, and colloids from water and groundwater. Neither method is suitable for the efficient removal of soluble As, but combining the microfiltration/ultrafiltration system with the adsorption system can improve the removal efficiency of As in water (Wan P et al., 2020). Nanofiltration is a high-pressure process, which removes large amounts of As from contaminated water (Singh R et al., 2015). In the natural water domain, the nanofiltration membrane can effectively remove As(V), and to remove As(III), the pre-oxidation process needs to be increased. Recently, Figoli A et al. (2020) applied a nanofiltration device to As(V) remediation of contaminated groundwater. The concentration of As in treated groundwater was less than 10  $\mu\text{g/L}$ , which confirms that nanofiltration is a suitable technique for remediation of groundwater with high As contents. Finally, reverse osmosis is a technology based on membrane separation to reduce various solutes in water. Reverse osmosis can remove 80% to 99% of As(V) in water (Schmidt SA et al., 2016).

### 6.3. Biological treatment

Microbial remediation of As in water is an efficient, low-cost, and environmentally friendly method. Microbial remediation of As includes microbial oxidation, biological adsorption and methylation, and microbial mediated As REDOX reaction is one of the most important processes in As remediation. Researchers found a unique lactic acid micro bacterium that can tolerate up to 3000 mg/L arsenites and rapidly oxidize As(III) to As(V), which can be used in field bioremediation of As-contaminated areas (Zheng Z et al., 2012). Several mechanisms of As transformation exists in cyanobacteria and other algae, including oxidation and methylation of As(III) (Ye J et al., 2012), reduction of As(V) (Wang Y et al., 2015) and biosynthesis of toxic lipid and toxic granulated sugar (Xue XM et al., 2017). Despite the toxicity of As, these algae are tolerant to high levels of As and have attracted considerable attention As a promising alternative for As removal (Zhu F et al., 2020).

### 6.4. Nanocomposites

Nano-scale adsorbents (Zeolite Imidazole Framework, referred to as ZIFs) are an emerging class of new adsorbents, which have been widely used in the field of remediation of As pollution in the environment (Massoudinejad M et al., 2018). ZIFs nanoparticles are porous crystal polymers formed by organic imidazole ligands and zinc ions (Evans HA et al., 2020), which have high chemical stability, ultra-high porosity,

and thermal stability in water (Park KS et al., 2006; Wang B et al., 2008). Jian M et al. (2015)'s research on the capture and adsorption of As by ZIF-8 nanoparticles showed that ZIF-8 nanocrystals could rapidly adsorb As(III) and As(V) at room temperature. Therefore, ZIF-8 nanoparticles have great application potential in the field of As.

Metal oxide nanoparticles with high specific surface area and multiple hydroxyl groups play an important role in removing contaminants from water (Hayati B et al., 2018). Copper oxide nanoparticles (CuO) perform well in the presence of competing anions and do not require pH adjustment or oxidation of As(III) to As(V) (Martinson CA et al., 2009). Kumar I et al. (2020) studied the removal of As(III) from polluted water by CuO nanoparticles, and the results showed that when the initial concentration was 100  $\mu\text{g/L}$ , 200  $\mu\text{g/L}$ , 500  $\mu\text{g/L}$ , and 1000  $\mu\text{g/L}$ , removal rates of As(III) were 97.8%, 94.6%, 91.5%, and 88.4%, respectively. The results showed that CuO nanoparticles could efficiently remove arsenite from water.

### 6.5. Electrochemical

Electrochemical technology is also an economical and feasible method for As removal. When a current is applied to the two electrodes, Fe(III) ions will be produced continuously and rapidly hydrolyzed in solution to form various forms of iron (hydrogen) oxide, which has a very high affinity with As(V) and can remove As from water (Asere TJ et al., 2019). Meanwhile, more toxic As(III) is oxidized *in situ* to As(V) and subsequently combined with iron (hydrogen) oxides (Rathi BS et al., 2021). Results showed that the device was able to reduce As concentrations in groundwater in Bangladesh from 200  $\mu\text{g/L}$  to below the WHO limit of 10  $\mu\text{g/L}$  (Ashraf S et al., 2019).

In addition, permeable reactive barrier (PRB) technology is an economical and practical groundwater remediation technology, which can replace traditional groundwater remediation systems to treat As contaminated groundwater. Thermodynamic studies show that zero-valent iron has a high adsorption capacity for As(V) and As(III), and is considered an effective material for removing As (Alsulaili A et al., 2020; Nriagu J et al., 2018). In addition, biochar, nano-sized iron oxide particles, fly ash, microorganisms, alumina, activated carbon and other substances have been used in PRB to adsorb As compounds in the environment (Sharma VK et al., 2009; Saunders JA et al., 2008).

In summary, all methods can remove As from groundwater and drinking water relatively effectively and sustainably. However, all methods have certain limitations. Therefore, the development of materials with higher As removal performance and sustainability still needs joint efforts of scientists and governments of various countries.

## 7. Conclusions

The main conclusions of this paper are as follows:

- (i) There are three main natural sources of As in

groundwater: hydrothermal activities, ore deposits, and Cenozoic sediments. Among them, As in aquifer sediments in different regions of China is the main source of As in groundwater with high-As content.

(ii) The high-As groundwater in China is mainly distributed in the inland basins in arid and semi-arid environments and reductive aquifers in the river deltas in humid environments.

(iii) The main formation mechanism of high-As groundwater is the reduced dissolution of iron and manganese oxides under the action of organic matter and native microorganisms. An alkaline environment, strong evaporation, long-term water-rock interaction, and slow groundwater flow rate promote continuous migration and enrichment of As in groundwater.

(iv) Arsenic has unique physical and chemical properties that can cause acute or chronic poisoning, which has also been shown to be a genetic toxin. Chronic symptoms caused by long-term exposure to As are non-specific, and its chronic toxicity can adversely affect the entire multi-organ system. Arsenic is absorbed in the digestive tract and transported through the bloodstream to body tissues. Inorganic As entering the body is metabolized through a combination of methylation (detoxification) and reduction (activation), catalyzed by a series of methyltransferases and reductases, respectively.

(v) The relatively mature treatment methods mainly include ion exchange technology, membrane filtration technology, biological treatment technology, nanocomposite adsorption technology, electrochemical technology, etc. All of the above methods can be relatively effective in removing As from groundwater and drinking water, but all of them still have certain limitations. It is urgent to develop remediation methods and technologies with higher As removal performance and sustainability. The high concentration of As in groundwater threatens the life and health of millions of people all over the world. It is hoped that with the joint efforts of scientists and governments around the world, As-poisoning in drinking water can be solved as soon as possible.

#### **CRedit authorship contribution statement**

Zhen Wang and Hua-ming Guo conceived the presented idea. Zhen Wang wrote the manuscript with support from Hua-ming Guo, Hai-yan Liu, and Wei-min Zhang. All authors provided critical feedback and helped shape the research, analysis, and manuscript.

#### **Declaration of competing interest**

The authors declare no conflicts of interest.

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