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Hydrogeochemical Characteristics of Areas with Arsenic Poisoning from Drinking Water and Arsenic Enrichment in Groundwater in Songnen Plain of China

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The aim of this study was to statistically analyze the environmental characteristics of groundwater of the Songnen Plain, China, which is elevated in arsenic and used as drinking water. Topographical, geological and hydrogeological conditions of the study area were evaluated along with regional geochemical survey results and previous epidemiological surveys and a field investigation was conducted in which 196 groundwater samples were collected and analyzed. Descriptive statistics, contouring and correlation analyses were calculated for the main chemical components (arsenic and fluorine) of concern in the groundwater. Analysis of regional hydrological geochemical characteristics, arsenic concentrations and distribution in the groundwater, correlations of arsenic with other elements in the groundwater and hydrochemical factors associated with enrichment of arsenic were determined. The results showed that the As^{5+} concentration ranged over 0.00024-0.33604 mg/L, higher than that of As^{3+} and in tertiary and quaternary confined water exceeding the drinking water standard of 0.01 mg/L. High arsenic concentrations in groundwater corresponded to high concentrations of total iron and bicarbonate, low concentrations of sulphate and a higher ratio of Na/(Cl + SO$_4$) meq. Groundwater with high arsenic was generally of the HCO$_3$, HCO$_3$-Cl, or Cl-HCO$_3$ type. Enrichment of arsenic in groundwater is influenced by many factors, the two most significant of which are geological sources and hydrochemical conditions.

Keywords: Arsenic, Songnen plain, Hydrochemical characteristics, China, Enrichment law.

INTRODUCTION

Arsenic poisoning results in systemic chronic illness characterized by skin pigmentation and depigmentation, diverse adverse health effects on metabolism and organs and cancer and is caused by excessive intake of arsenic through drinking water, air and/or food over the long-term. Arsenic poisoning is widely distributed globally, with varying incidence in more than 20 countries and many studies of arsenic poisoning have been carried out. Arsenic poisoning can be related to drugs, environmental contamination, occupational exposures, or natural biogeochemical sources.

Biogeochemical arsenic poisoning refers to that caused by the natural environment or non-anthropogenic factors and mainly results in chronic exposures. It frequently occurs in areas with hot springs, such as the volcanic hot springs in Japan, New Zealand, *etc*. Biogeochemical arsenic poisoning has been reported in Oregon, USA; Taiwan, Xinjiang and Inner Mongolia, China; and other areas[1,2].

China has a vast territory with a complex natural environment. Arsenic poisoning from drinking water in China is widely distributed and is greatly harmful to human health. Studies have documented arsenic poisoning from drinking water in Taiwan, Xinjiang, Inner Mongolia, Shanxi, Jilin, Anhui and 8 other provinces (autonomous regions) and 40 counties (banners and cities). About 230 million people have been exposed, of which 500,000 have drinking water with > 0.05 mg/L arsenic and nearly 7821 people have been documented to have arsenic poisoning[3]. Systematic studies have been carried out in areas with widespread arsenic poisoning, summarising the pathogenesis and the hydrochemical characteristics in these regions[4-7,1].

Drinking water is the main source of arsenic poisoning in the environment. Arsenic in drinking water may be natural (endemic) or from anthropogenic pollution and regardless of the source, most people drink the high-arsenic ground water. The incidence of arsenic poisoning is related to the environmental characteristics of the local water and soil, as well as the quality of the drinking water, particularly total arsenic, As^{3+} and organic arsenic concentrations in the water.

Transport and enrichment of arsenic in groundwater are closely related to the depositional environment, hydrogeological conditions and hydrochemical environment. Its distribution is frequently associated with depositional environments. Based on the distribution of sedimentary environments[1] divided areas in China with arsenic poisoning into three types, the Cenozoic rift basin, the Cenozoic coastal plain and Quaternary alluvial plains. Among these, Inner Mongolia, Shanxi and Jilin with the largest area and sphere of influence are representative of the Cenozoic rift basin; Chiayi in southern Taiwan is representative of the Cenozoic coastal plain type and Kuitun in Xinjiang is representative of the Quaternary alluvial plain type.

Songnen plain is a large rift basin formed during the Mesozoic and Cenozoic periods. To the west is the hilly tableland of the eastern foothills of the Xiaoxinganling Mountains. To the north are the Xiaoxinganling mountains and to the east, the tableland foothills of the Changbai Mountains. To the south is the uplift zone of the Songliao watershed[8-10]. The arsenic in the groundwater of this area is affected by the climate and geology and exceeds the drinking water standard, resulting in widespread endemic arsenic poisoning in the local district.

Arsenic poisoning was first identified in western Jilin Province in 2002. It is mainly distributed in Tongyu and Taonan Counties, where the residents use the phreatic groundwater as their primary source of drinking water, while others drink the confined groundwater. An epidemiological endemic arsenic poisoning investigation was conducted during 2002-2005 by the Endemic Disease First Prevention Institute of Jilin Province. Of the 4903 people surveyed (2415 men and 2488 women), 93 were found to have stumbling, keratosis, chapped skin and skin pigmentation to differing degrees. These individuals accounted for 1.90 % of those surveyed, of which the youngest was 6 years old and the oldest was 80 years old. The local residents suffered from arsenic poisoning as well as fluorosis, with accompanying physical and mental health risks[11].

By analyzing the common features of arsenic poisoning in each area of China, it has been observed that arsenic poisoning frequently results from the local residents changing their original drinking water sources, rivers and shallow groundwater with low concentrations of arsenic, to deep groundwater sources with high arsenic. After 5-10 years of exposure, arsenic poisoning begins to cause health effects.

The sedimentary environment of the Songnen plain has a complex groundwater environment. The present study of the characteristics of the groundwater environment in this area provides information on the origin of the high arsenic concentrations in groundwater and influencing factors, providing a scientific basis for disease prevention and water resource improvement.

Study area: Songnen plain is one of three major plains in northeast China, with a total area of 182,800 km^2. It is part of the large Songliao Mesozoic-Cenozoic rift basin, composed of 8000-m-thick continental sediments with oil deposits[10]. The plain is an asymmetric semi-enclosed basin extending NNE in the form of a diamond, higher in elevation along the four sides and lower in the middle, gently inclined from the periphery to the centre. The terrain can be divided into three areas, including the eastern high plains, central low plains and western piedmont sloping plains. The eastern high plains and the western Daxinganling sloping piedmont plains are discharge areas for mountain bedrock fissure water, as well as the main recharge areas for the central artesian water basin. North, east and south of the plain are uplift zones, to the west is a sloping zone and in the centre is a large depression acting as a water storage basin consisting of quaternary phreatic and confined groundwater and Tertiary confined groundwater[10].

Based on regional geomorphological characteristics, the Songnen plain can be divided into four hydrogeological units, including the eastern high plains, the central low plains, the western daxinganling sloping piedmont plains and the valley plains[10]. The high plains are dominated mainly by loess-like loam with low permeability and strongly sloping terrain, not conductive to groundwater retention and with little phreatic water. The low plains in the centre have a multilayer structured aquifer system consisting, from lower to upper layers, of a confined aquifer in the Tertiary Eocene-Oligocene Yi'an group, a confined aquifer in the Miocene Da'an group, a confined aquifer in the Pliocene Taikang group and quaternary lower pleistocene and phreatic groundwater in the upper alluvial aquifer. The piedmont in the west Songnen plain is a highly productive groundwater aquifer consisting of a gravel alluvial fan with substantial groundwater storage. The groundwater in this area flows horizontally from the eastern high plains and the western piedmont sloping plains to the low plains in the centre. The confluence of the Songhua river and the Nen river is a collection area for regional groundwater. The groundwater then flows along the Songhua river valley to the northeast and discharges outside the region. Vertically, phreatic groundwater in porous sediments and confined groundwater flow downward to recharge the Tertiary-Quaternary Taikang confined aquifer. The Tertiary Da'an group, Yi'an group and Cretaceous confined groundwater aquifers recharge the Taikang confined groundwater aquifer through upward flow. Songnen Plain represents a typical topography with mountainous recharge areas, valleys and a piedmont alluvial fan as runoff areas and low plains and a lacustrine centre as runoff and discharge areas. The main groundwater depletion processes include evaporation, lateral runoff, discharge of groundwater into the rivers and manual extraction[4,12,14] (Fig. 1).

Under the influence of the natural environment, geology and human activities and with recharge, runoff and discharge of groundwater, the various chemical constituents in the groundwater of Songnen plain are constantly changing in complex ways through leaching, migration and aggregation. The primary anion in the groundwater in each aquifer is bicarbonate, with sulphate, chloride and nitrate distribute locally. The main cation in the phreatic water is calcium, followed by nitrate and magnesium and the main cation in the confined water is nitrate, followed by calcium and magnesium[4,12,13].

West Jilin Province in the southwest Songnen Plain is the main area experiencing arsenic poisoning, mainly distributed in Tongyu and Taonan Counties. The area has a northern temperate semi-arid continental climate. As a part of the massive Mesozoic and Cenozoic Songliao rift basin, a 5000-m-thick inland lacustrine deposit is present, forming a very large and complex aquifer system, including Quaternary porous phreatic and confined aquifers, porous and fractured confined aquifers of the upper Tertiary Da'an and Taikang group and a Cretaceous fractured porous confined aquifer[4,12,13].

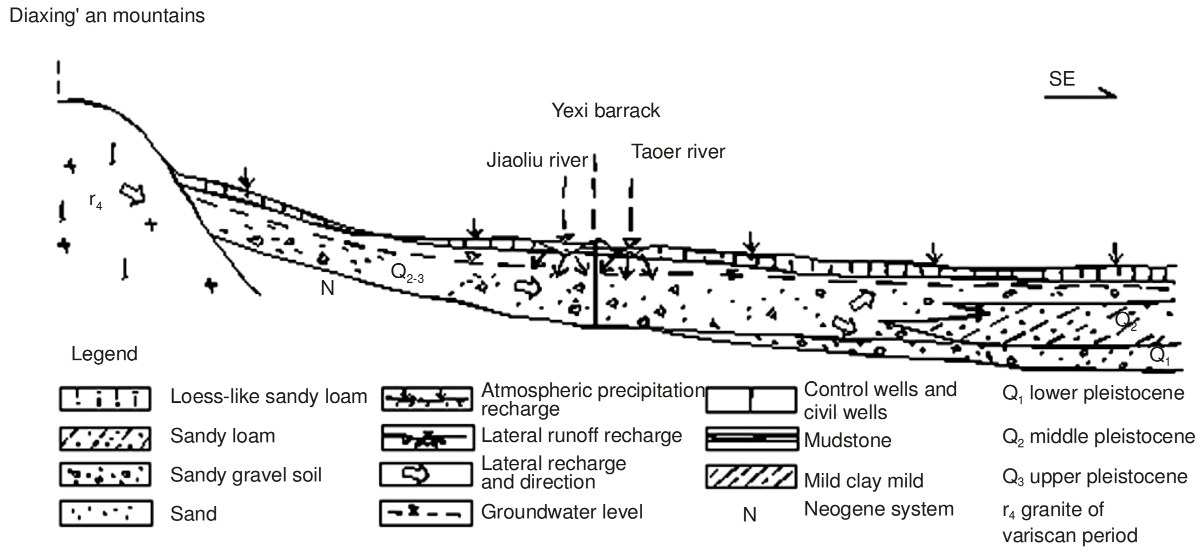

Fig. 1. Hydrogeological profile in the study area

EXPERIMENTAL

Sample collection: Based on the topography, geology and hydrogeology of the study area combined with previous regional geochemical survey data and epidemiological data, a field survey and subsequent collection of 196 groundwater samples were carried out in June-July 2006 and in July-August 2007, respectively. The locations of the sampling stations are shown in Fig. 2.

Sample bottles for instantaneous water sampling were soaked with 10 % HNO_3 for 3 days before sampling and then rinsed with running water and distilled water. The sample bottles

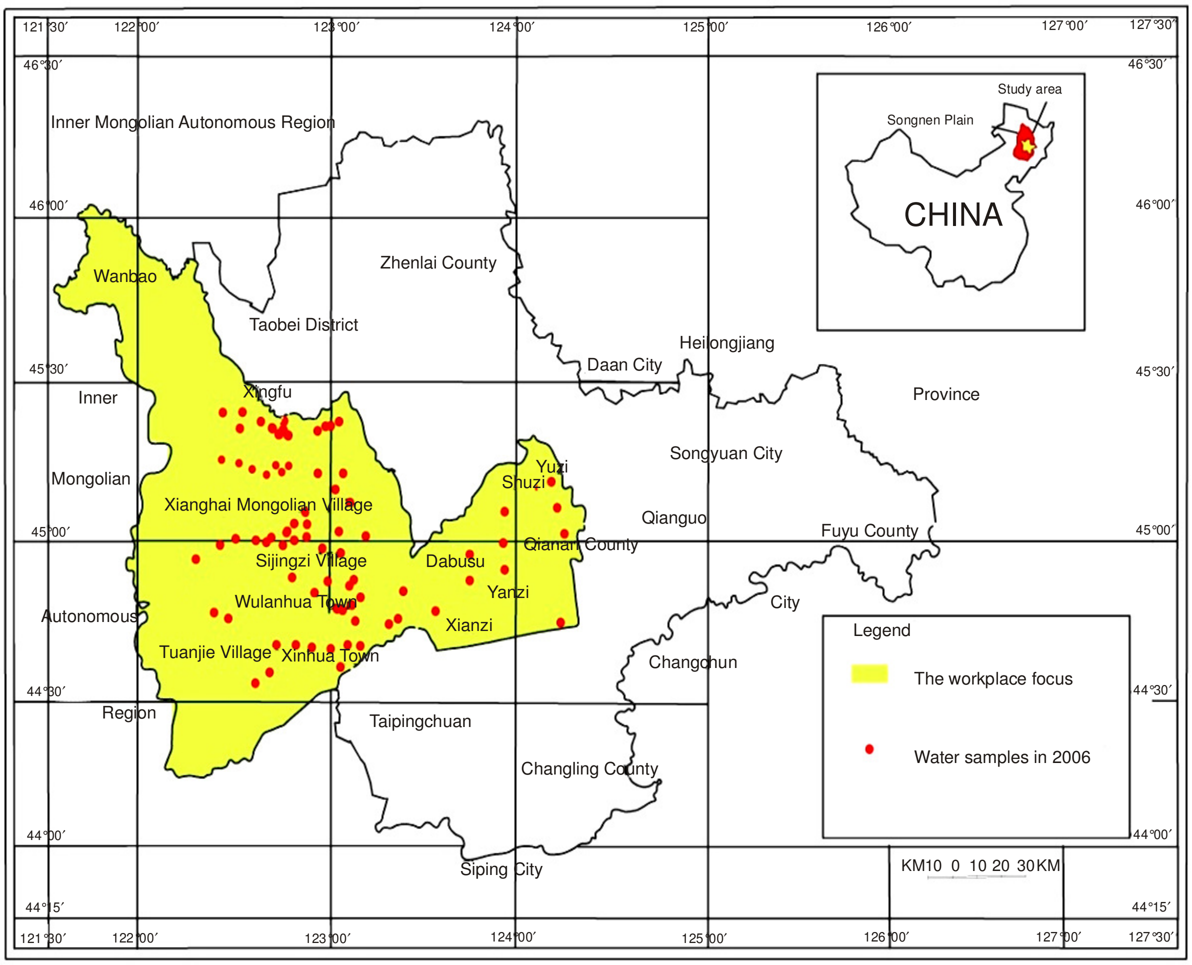

Fig. 2. Locations of groundwater samples

and stoppers were washed 3-5 times with the water to be sampled before sampling, followed by addition of 10 mL (1+1) HNO_3 and then shaken. The samples were stored in 1.5 L polyethylene plastic bottles with an inner plug screw and wax seal.

Test methods and accuracy: The water samples were tested for 26 analytes, among which the major elements (Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, PO_4^{3-}, NO^{2-}, Ca^{2+}, Mg^{2+}, total hardness, *etc.*) were analyzed by the volumetric method, F^- was analyzed with an ion-selective electrode and K^+ and NH_4^+ were analyzed by spectrophotometry with a detection limit of 0.01 mg/L. Total arsenic, As^{3+} and As^{5+} were analyzed by atomic fluorescence spectrometry with a detection limit of 0.001 mg/L. Plasma mass spectrometry was used to analyse Cu and Zn with a detection limit of 0.001 mg/L. Se and total Fe were analyzed by atomic absorption spectrometry with a detection limit of 0.01 μg/L.

Date analysis: The statistical analysis software SPSS 14.0, kriging interpolation, geographic information system software MapGIS and drawing software Surfer were used to develop descriptive statistics and correlation analyses for the concentrations of the main chemical components in the groundwater and to draw contours of the fluorine and arsenic concentrations in the groundwater.

RESULTS AND DISCUSSION

Regional hydrological geochemistry: The groundwater of the Songnen plain is controlled by topography, lithology, hydrometeorology, soil, vegetation and other natural factors. The groundwater has a complex chemical composition and various hydrochemical types[4], shown in Table-1.

TABLE-1
HYDROCHEMICAL TYPE OF PHREATIC WATER HORIZONTAL ZONATION TABLE

Hydrogeology units	Western piedmont sloping plains	Central low plains	Eastern high plains
Major water chemical types	HCO_3-Ca HCO_3-Ca, Mg HCO_3-Ca, Na	HCO_3-Na HCO_3-Na, Mg HCO_3-Na, Ca HCO_3-Cl-Na HCO_3-Cl-Na, Mg SO_4-HCO_3-Na Cl-NO_3-Na Cl-NO_3-Na, Mg	HCO_3-Ca HCO_3-Ca, Na HCO_3-Ca, Mg NO_3-Ca, Mg HCO_3-NO_3-Ca

Hydrochemical differences follow the direction of groundwater flow, from the uplifted eastern high plain and western inclined piedmont plain to the sustainable settlements in the central low plain, from hydrological alteration dominated by leaching to slow groundwater alteration dominated by concentration through evaporation and alternate adsorption of cations. The elements in the eastern high plain and western inclined piedmont plain easily disperse and do not concentrate, forming a low-iodine area. In contrast, the elements in the central low plain are concentrated and do not easily disperse, forming high-fluorine groundwater and high-salinity soil.

In the main agricultural areas, such as the eastern high plains and central low plains, nitric groundwater was present to varying degrees, resulting from long-term use of fertilizers in agricultural production, contaminating the groundwater. Near dense population centres and towns with industrial development, particularly those with industrial sewage, phreatic groundwater was contaminated, the chloride content was higher and bicarbonate-chloride groundwater was observed. These effects were most apparent around Harbin, Changchun and Shuangcheng. In addition, in the southern Nen river and nearby Songhua river valley plains near Harbin, large amounts of wastewater containing sulphides are discharged from industries, resulting in bicarbonate-sulphate groundwater.

The Pleistocene confined aquifer and the confined aquifer below it in the eastern high plain are not deeply buried and have semi-open weakly reducing environments; therefore, the hydrochemical type was dominated by HCO_3-Ca, followed by HCO_3-Ca/Mg, HCO_3-Ca/Na and HCO_3-Na/Ca. The salinity was 0.24-1.05 g/L, the pH was 6.5-8.3 and the total hardness was 1.78-8.17 meq/L.

The strata formed in the tertiary Pliocene and quaternary Baitushan group were deposited in an arid and cold climate in the central low plain, conductive to soda salinization in the sediments and groundwater. In addition, the groundwater in the centre of the basin moves slowly, resulting in a primary groundwater type of HCO_3-Na, followed by HCO_3-Na/Ca and HCO_3-Ca/Na. From the confined aquifers surrounding the basin to the centre, the hydrochemical type was cyclically distributed-east, north and west had HCO_3-Ca/Na, HCO_3-Ca and HCO_3-Ca/Mg groundwater types, respectively. HCO_3-Na/Ca (or HCO_3-Na/Mg) groundwater was found in the intermediate area between the boundaries and the centre of the basin and HCO_3-Na, HCO_3-SO_4-Cl-Na/Mg and HCO_3-Cl-Na/Mg were found in the centre of the basin. The salinity was 0.15-3.53 g/L, the pH was 6.6-8.8 and the total hardness was 0.41-17.47 meq/L.

Arsenic concentrations and distribution in groundwater: As a toxicological index, the Chinese drinking water standard for arsenic is 0.01 mg/L (No. 2006) and the arsenic standard for small centralized and decentralized water supplies is 0.05mg/L. Generally, arsenic in water exists in inorganic[1,2,11] and organic forms, including As^{5+}, As^{3+}, methyl arsine and dimethyl arsine. The focus of our analysis was the distribution of As^{3+} and As^{5+} in the groundwater (Table-2). The rate of arsenic metabolism is related to the morphology and valence state of the arsenic. The metabolism of As^{5+} is faster than that of As^{3+} and As^{5+} is also 60-100 timesless toxic than As^{3+} in groundwater. In areas with a high incidence of arsenic poisoning, the valence state of arsenic in groundwater is fairly consistent.

TABLE-2
COMPARISON OF As^{3+} AND As^{5+} IN THE STUDY AREA

		As^{3+}	As^{5+}
Phreatic water	Average (mg/L)	0.00221	0.01694
	Range (mg/L)	0-0.02458	0-0.1543
	As^{3+}/As^{5+}	1/7.67(0.13)	
Quaternary confined water	Average (mg/L)	0.00647	0.03622
	Range (mg/L)	0-0.0385	0-0.13449
	As^{3+}/As^{5+}	1/5.60(0.2)	
Neogene confined water	Average (mg/L)	0.00175	0.01638
	Range (mg/L)	0-0.00978	0-0.33604
	As^{3+}/As^{5+}	1/9.36(0.11)	

The As^{3+} concentrations in the groundwater were lower (0-0.00813 mg/L) than the As^{5+} concentrations (0.00024-0.33604 mg/L). High-arsenic groundwater was mainly found in the confined aquifers. The As^{3+} and As^{5+} concentrations in the tertiary and quaternary confined aquifers were clearly higher than those in the phreatic groundwater. The mean As^{5+} concentration in the tertiary and quaternary confined groundwater generally exceeded the drinking water quality standard of 0.01 mg/L.

Arsenic concentrations exceeded the 0.01 and 0.05 mg/L drinking water standards in 43.1 % and 16.49 % of the groundwater samples, respectively. The arsenic concentrations in the groundwater of Tongyu exceeded the drinking water standards, while they were lower in Taonan and Qianan, exceeding the groundwater standards only in certain local areas. Groundwater with > 1 mg/L arsenic was mainly distributed in Xinxing, Tongyu County and the area around Sijingzi along the Huolin river (Fig. 3).

From Tongyu to Taonan and Qianan, *i.e.*, from the northwest piedmont alluvial plain to the alluvial fan front to the lower plain area, the ground water chemistry gradually changed to a highly mineralized reducing environment, with less leaching and greater evaporation[9]. The flow from west to east is blocked by the Xiangyang, Fuxing and Dabusu uplifts in the middle of the basin, which slows the runoff down. As a result, the groundwater chemistry transitioned from HCO_3-Ca to HCO_3-Na·Mg and HCO_3-Ca·Na; total dissolved solids, As, Fe, Mn, Cl-, PO_4^{3-} and HCO_3^- increased; and SO_4^{2-} and Se decreased. Groundwater with high concentrations of As was mainly distributed along the Huolin river and the Taoer river, including south Taonan and east-central Tongyu.

Vertically, samples with arsenic above the drinking water standard were mainly collected from 50-80 m deep in the aquifer (Table-3) with an exceedance rate of > 40 %, with some samples exceeding the standard above and below that depth at 10-100 m deep. At < 10 m in shallow groundwater, there were only a few samples exceeding the standard and the mean As concentration was 0.00751 mg/L, below 0.01 mg/L. At 100-150 m deep in the Tertiary confined aquifer, the mean arsenic concentration was 0.03505 mg/L (0.00121-0.33904 mg/L). Exceedance of the drinking water standard were not found at > 150 m depth in the groundwater. More attention should be paid to the 20-80 m deep sections of the aquifer with the highest exceedance rates, in which the mean and maximum concentrations of arsenic are also higher than at other depths.

Correlations between arsenic and other elements in the groundwater: The relationships between high arsenic concentrations and other elements in the groundwater are shown in Table-4. High arsenic concentrations in groundwater were associated with high total iron, bicarbonate and Na/(Cl + SO_4) meq ratio and with low sulphate. The correlation coefficients for these and the other elements are shown in Table-5.

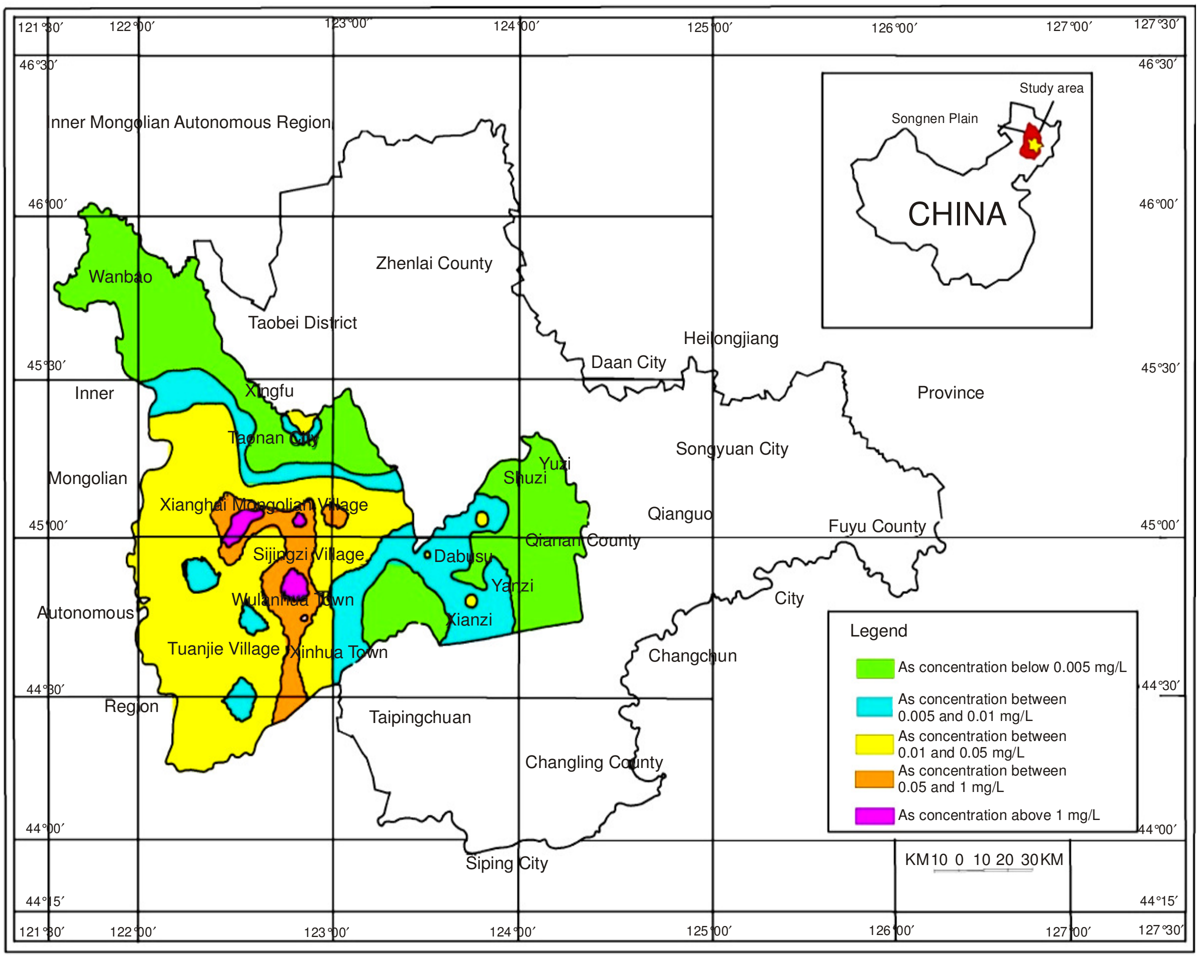

Fig. 3. Distribution of arsenic in groundwater in the study area

TABLE-3
CONTENT AND DISTRIBUTION OF ARSENIC IN GROUNDWATER OF DIFFERENT DEPTHS IN THE STUDY AREA

Ground water types	Well depth (m)	Well number	Range (mg/L)	Mean value (mg/L)	Standard value (mg/L)	Number of exceeded wells (number)	Exceeded rate (%)
Phreatic water	<10	17	0.00121-0.02599	0.00751	0.05	0	0.00
	10-20	42	0.00153-0.17888	0.02115	0.05	5	11.90
	20-40	38	0.00142-0.15698	0.01986	0.05	3	7.89
Quaternary confined water	40-50	10	0.00244-0.13433	0.02399	0.05	3	30.00
	50-80	36	0.0008-0.15241	0.04323	0.05	13	36.11
	80-100	20	0.0009-0.10968	0.0174	0.05	3	15.00
Neogene confined water	100-150	26	0.00121-0.33904	0.03505	0.05	5	19.23
	>150	5	0.00436-0.00881	0.00525	0.05	0	0.00

Note: According to the arsenic limit of Chinese drinking water standard in 2005 (No. 5749) on the small rural centralized and decentralized water supply, using the standard value 0.05 mg/L

TABLE-4
ENRICHMENT TYPES OF FLUORINE AND ARSENIC IN THE GROUNDWATER AND WATER CHEMICAL

Enrichment type	F^- (mg/L)	ΣAs (μg/L)	ΣFe (mg/L)	Mn (mg/L)	Ca^{2+} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	PO_4^{3-} (mg/L)	TDS (mg/L)	Na/(Cl + SO_4) meq	pH
High fluorine and high arsenic	1.96	98.67	1.85	0.23	49.18	25.6	676.67	0.3	872.4	5.86	8.87
High fluorine and compliance arsenic	3.18	4.378	0.68	0.26	58.33	53.13	501.88	0.29	902.54	3.03	8.92
High arsenic and compliance fluorine	0.88	163.8	3.01	0.14	63.49	11.83	605.59	0.2	556.73	7.28	8.57
Compliancefluorine and compliance arsenic	0.68	3.36	1.21	0.15	54.64	45.07	318.8	0.11	556.63	2.13	8.77

TABLE-5
ARSENIC AND OTHER CHEMICAL COMPONENTS PEARSON COEFFICIENT TABLE

	As	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	PO_4^{3-}	K^+	Na^+	Ca^{2+}	Mg^{2+}	TFe
As	1										
Cl^-	-0.201	1									
SO_4^{2-}	-0.523*	0.390	1								
HCO_3^-	0.645	0.161	0.363	1							
NO_3^-	-0.259	0.110	0.477*	0.313	1						
PO_4^{3-}	-0.230	-0.323	0.436	0.280	-0.019	1					
K^+	-0.002	0.014	-0.177	0.462	-0.330	0.321	1				
Na^+	-0.115	0.370	0.339	0.613**	0.584**	0.142	0.185	1			
Ca^{2+}	-0.052	-0.055	0.231	0.033	-0.164	0.267	0.182	0.205	1		
Mg^{2+}	-0.002	0.430	0.089	0.154	0.234	-0.141	0.112	0.496	0.402	1	
TFe	0.725**	-0.277	-0.315	0.213	-0.240	0.065	0.025	0.063	0.529	0.158	1

Note: The "**" in the upper right corner of the correlation coefficient in the above table represents a significant level of 1 %; the"*" in the upper right corner of the correlation coefficient represents a significant level of 1%

Studies in China and elsewhere have focused on the relationship between arsenic and iron, concluding that iron plays an important role in arsenic enrichment. Arsenic and iron concentrations in groundwater are often positively correlated. In Bengal[14,15], Fukuoka, Japan[15], the Chinese Hetao Plain and the Yangtze River Delta[16] where arsenic in the groundwater is high, iron and manganese concentrations are also high. Iron and manganese concentrations are relatively low in the high-arsenic groundwater of Shanyin County, Shanxi Province, due to production of H_2S through desulphationin a strongly reducing environment, promoting Fe^{2+} precipitation. The correlation coefficient between arsenic and iron in the present study was 0.725, indicating a strongly positive correlation.

High concentrations of biocarbonate are also conductive to accumulation of arsenic in groundwater; the correlation coefficient between biocarbonate and arsenic was 0.645. The sulphate concentration in high-arsenic water was significantly lower than that in groundwater that did not exceeding the drinking water standard (250 mg/L). A low concentration of sulphate reflects a strongly reducing groundwater environment. The correlation coefficient between sulphate and arsenic was -0.523, indicating a negative correlation.

The fact that arsenic in the groundwater is responsible for arsenic poisoning is indisputable. However, in different areas, due to the differences in water chemistry and the arsenic valence and chemical form, conditions affecting groundwater arsenic migration and transformation vary significantly. Hence, the relationship between arsenic concentrations in the groundwater and health effects due to arsenic also varies.

There were 62 of 196 samples containing high concentrations of fluorine and arsenic in groundwater, of which 56 can be classified as sodium carbonate groundwater, which is alkaline (pH > 8) with a water chemistry type of HCO_3, HCO_3-Cl, or Cl-HCO_3. The pH of higher sodium carbonate groundwater creates highly favourable conditions for release of arsenic from the sediments into the groundwater. In an oxidizing environment, arsenic is strongly adsorbed onto the surface of metal oxides (Fe, Al, Mn) and clay minerals. With an increase in pH, arsenic can desorb from the mineral surface into the groundwater. Total dissolved solids (TDS) in high-fluorine and high-arsenic groundwater were also very high, > 500 mg/L, mainly because the TDS concentration is high in the sodium carbonate area (Fig. 4).

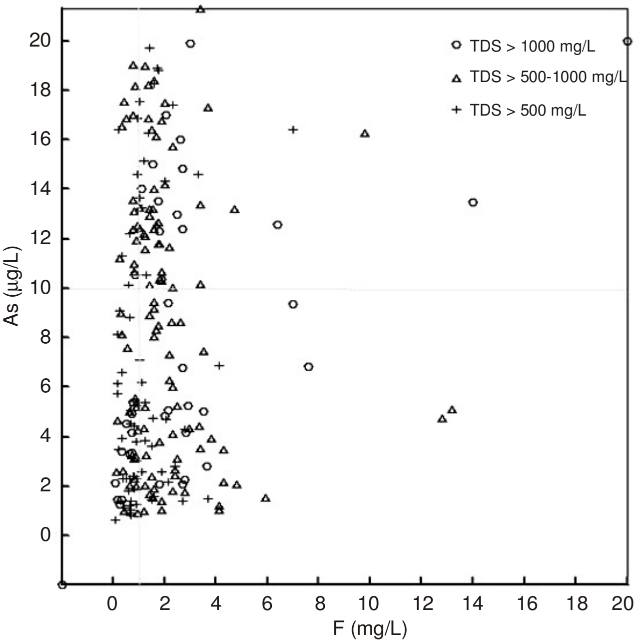

Fig. 4 Relationship between the fluorine and arsenic concentrations and the TDS content in groundwater

High-fluorine groundwater was often alkaline (pH > 8) with hydrochemical types of mainly HCO_3, HCO_3-Cl, or Cl^- HCO_3 (Figs. 5 and 6). The arsenic concentration was also high and the Na/(Cl + SO_4) meq ratio was generally > 1. Fluorine easily accumulates in high-sodium groundwater, in which there is a low concentration of calcium, due to the solubility limit of CaF_2. In addition, the biocarbonate-dominant alkaline environment is favourable for fluorine exchange from fluorine-containing minerals replaced by hydroxyl and released into the groundwater. Thus, as the Na/(Cl + SO_4) ratio increased, the concentration of fluorine also increased.

Based on these data, the concentrations of fluoride and arsenic in groundwater are closely correlated with the TDS content and hydrochemical nature of the groundwater. The TDS content was mainly > 500 mg/L in groundwater with high fluorine and arsenic, the hydrochemical types were mainly HCO_3, HCO_3-Cl, or Cl-HCO_3 and the meq ratio of Na/(Cl + SO_4) was generally > 1. Considering the formation conditions and characteristics of sodium carbonate water, it is a factor in the enrichment of fluorine and arsenic in the groundwater. The study area is the main area in China in which sodium-rich soil occurs and sodium is the dominant soluble salt in the soil. The soil has high levels of exchangeable sodium, which due to the interaction of water with the sediments and the effects of evaporative concentration, promotes formation of sodium carbonate-rich groundwater.

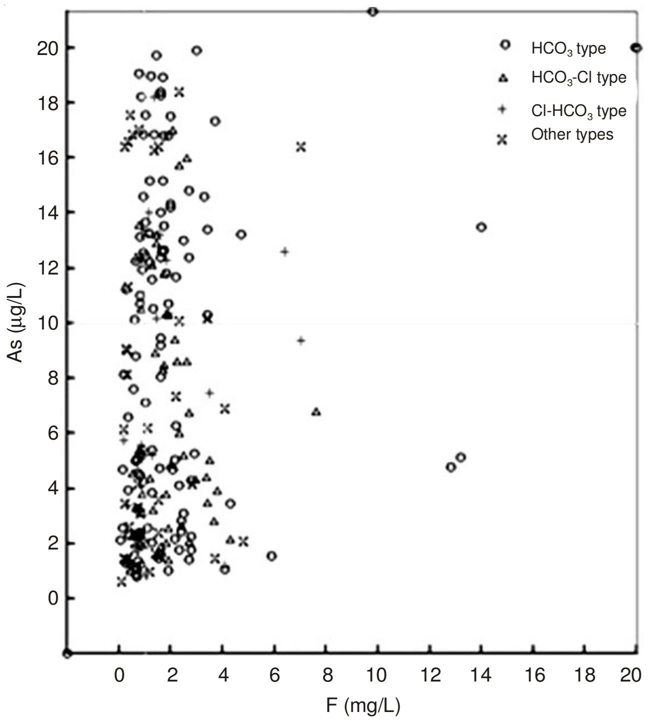

Fig. 5. Fluorine and arsenic concentrations and the hydrochemical type of the groundwater

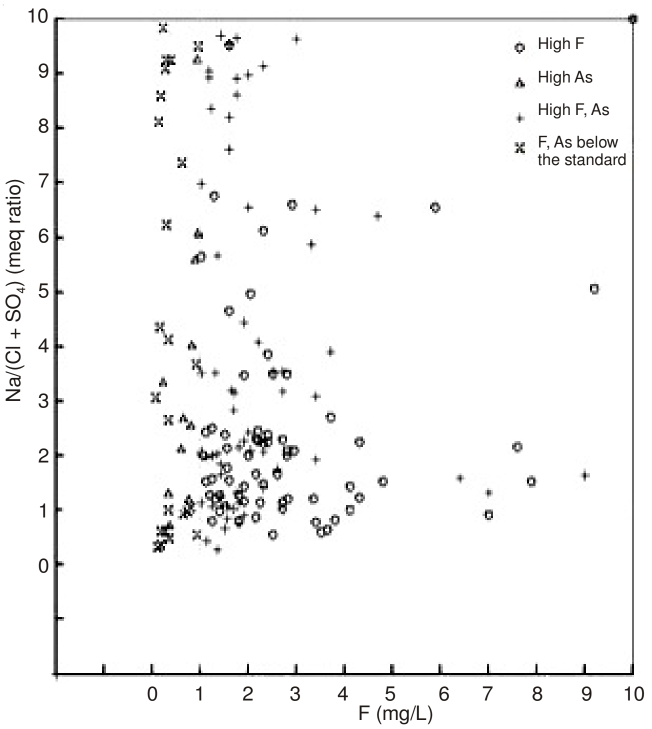

Fig. 6. Relationship between the fluorine concentration and Na/(Cl + SO_4)

Hydrochemical factors affecting arsenic enrichment in groundwater: Elemental enrichment in groundwater is influenced by many factors. The two most important of which are geological sources and hydrochemical conditions. The focus of this study was on analyzing factors affecting arsenic enrichment influenced by hydrochemical conditions within the known geological sources in the study area.

Adsorption-desorption reactions affect transport of As^{3+} and As^{5+} in the environment, with iron playing an important

TABLE-6
HYDROCHEMICAL INDICATORS COMPARATIVE TABLE OF ARSENIC EXCEEDED POINT AND NORMAL POINT

	ΣAs	ΣFe	Mn	HCO_3^-	SO_4^{2-}	NO_3^-	PO_4^{3-}	pH
Exceed points	0.05772	1.58	0.32	541.75	29.11	7.84	0.24	8.86
Normal points	0.00389	0.90	0.21	416.55	45.72	40.70	0.18	8.87

role in controlling arsenic concentrations. The groundwater data for this area indicate that the mean iron concentration in high-arsenic groundwater is higher than that in areas that do not exceed the drinking water standard (Table-6). Iron hydroxide strongly absorbs cations and anions, having functional groups consisting of positively charged iron ions and negatively charged hydroxyl groups, which can absorb arsenic.

pH is an important factor controlling the state and activity of arsenic in groundwater. The solubility of arsenic increases with pH and high pH also promotes desorption of arsenic. The study area is located in an arid to semi-arid area. Evaporative concentration raises the pH to 8.10-9.30, an alkaline environment conductive to desorption of arsenic. Alkalinity of the groundwater is a common feature of high-arsenic aquifers in basins, such as Shanxi Datong with a pH of 8-9. The arsenic concentration in the Hetao Plain of Inner Mongolia has also been reported to have a positive correlation with pH[4].

In an oxidizing environment, arsenic compounds in groundwater (arsenate or arsenite) are adsorbed by colloidal ferrimanganic oxide or hydroxide, resulting in very low concentrations of arsenic in the groundwater. However, in a reducing environment, the colloids become unstable and the ferrimanganic hydroxide is reduced, desorbing arsenic into the groundwater. Globally, high arsenic concentrations in groundwater are generally found in reducing environments.For example, high arsenic concentrations in shallow groundwater were found with high concentrations of DOC, HCO_3^-, NH_4^+ and sulphide and low concentrations of nitrate and sulphate, as well as high methane gas contents in some local areas of the Hetao plain of Hangjinhou Banner, Inner Mongolia[3]. At the Hetao plain, high-arsenic groundwater and the sediments in the aquifer nearly all had a strong odour of hydrogen sulphide while sampling and the water from the hand pressure well could be ignited[1,2]. Similar conditions were not found in our study area, but the high concentration of HCO_3^- and low concentration of sulphate in the groundwater that exceeded arsenic drinking water standards indicates a reducing environment in the aquifer; however, the degree of reducing potential is weaker than in other high-arsenic areas.

The redox condition is the main factor influencing the valence of arsenic. Reduction transforms AsO_4^{3-} into AsO_3^{3-}. As^{5+} is dominant in oxygen-enriched groundwater, but arsenic is mainly present as As^{3+} under reducing conditions. The toxicity of As^{3+} is 60-100 times that of As^{5+} and is the main form of arsenic in groundwater related to arsenic poisoning. To some extent, the ratio of As^{3+} to As^{5+} in groundwater also reflects the redox condition. Thus, comparing the data for this project with the total arsenic and As^{3+} concentrations in the groundwater of the Hetao plain in Inner Mongolia and of the Datong basin in Shanxi, we found that the ratio of total arsenic to As^{3+} in Inner Mongolia and the Datong basin was significantly higher than that in this region (Table-7).

TABLE-7
As(III) STATISTICAL RESULTS TABLE OF THE
MAIN ARSENIC POISONING AREAS IN CHINA

		Songnen plain	Hetao plain	Datong basin
ΣAs (μg/L)	Rage	0.8-339	0.6-653	4-1112
	Mean	25.3	89.0	115.2
As(III)/ΣAs (%)	Range	0-100	21-96	25-91
	Mean	32.4	90	72

Conclusions

- Fluorine concentrations in the groundwater of Songnen plain were highest in the basin centre and decreased towards the edge of the basin. The fluorine concentration was also highest in the shallow phreatic groundwater and decreased in the deeper confined aquifers. Unlike fluorine, high concentrations of arsenic were present only in specific geological environments and were concentrated at 50-80 m depth in the aquifer.
- The As^{3+} concentration in the groundwater in the study area was low (0-0.00813 mg/L) and the As^{5+} concentration relatively high (0.00024-0.33604 mg/L). The average As^{5+} concentration in the tertiary and quaternary confined aquifers exceeded the drinking water standard of 0.01 mg/L.
- High concentrations of arsenic in groundwater were found with high total iron and bicarbonate, low sulphate and an $Na/(Cl + SO_4)$ meq ratio > 1. Groundwater with high fluorine concentrations was characterized by a high concentration of TDS, nearly twice as much as that in groundwater with typical fluorine concentrations. High-fluorine and high-arsenic groundwater was mainly of the HCO_3, HCO_3-Cl, or Cl-HCO_3 type.
- High concentrations of arsenic in groundwater are affected by many factors. The two most important of which are the geological origins and water chemistry. The average iron concentration in groundwater with high levels of arsenic was much higher than that in areas that were below the drinking water standard. Alkaline environments such as found in the study area are conductive to arsenic desorption, which can increase arsenic concentrations in the groundwater.

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