Hydrogeological and biogeochemical constrains of arsenic mobilization in shallow aquifers from the Hetao basin, Inner Mongolia

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Both hydrogeologic conditions and biogeochemical processes control As distribution of shallow groundwaters, which results in the occurrence of low As groundwater in alluvial fans and near irrigation channels and drainage channels.

\textbf{ARTICLE INFO}

Article history:
Received 3 August 2010
Received in revised form 21 December 2010
Accepted 22 December 2010

Keywords:
Arsenic
Dissolved organic matter
Groundwater
Hydrogeochemistry
Isotope

\textbf{ABSTRACT}

Little is known about the importance of drainage/irrigation channels and biogeochemical processes in arsenic distribution of shallow groundwaters from the Hetao basin. This investigation shows that although As concentrations are primarily dependent on reducing conditions, evaporation increases As concentration in the centre of palaeo-lake sedimentation. Near drainage channels, groundwater As concentrations are the lowest in suboxic-weakly reducing conditions. Results demonstrate that both drainage and irrigation channels produce oxygen-rich water that recharges shallow groundwaters and therefore immobilize As. Groundwater As concentration increases with a progressive decrease in redox potential along the flow path in an alluvial fan. A negative correlation between \(\text{SO}_4^{2-}\) concentrations and \(\delta^{34}\text{S}\) values indicates that bacterial reduction of \(\text{SO}_4^{2-}\) occurs in reducing aquifers. Due to high concentrations of \(\text{Fe}^{2+}\) (>0.5 mg L\(^{-1}\)), reductive dissolution of Fe oxides is believed to cause As release from aquifer sediments. Target aquifers for safe drinking water resources are available in alluvial fans and near irrigation channels.

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1. Introduction

High As groundwaters have been found in many parts of the world, especially Asian countries, e.g., Bangladesh (Nickson et al., 1998; Harvey et al., 2002), India (McArthur et al., 2004; Roychowdhury et al., 2005; Chauhan et al., 2009), China (Smedley et al., 2003; Guo et al., 2008a), Pakistan (Nickson et al., 2005), Nepal (Gurung et al., 2005), Cambodia (Polya et al., 2005) and Vietnam (Berg et al., 2001; Postma et al., 2007). The groundwater As is of geogenic origin and considerably patchy on a local scale (Harvey et al., 2002; Ng et al., 2003; van Geen et al., 2003; McArthur et al., 2004; Guo et al., 2008a).

Many studies have been done concerning geological, hydrological, geochemical, hydrogeochemical, mineralogical and biogeochemical aspects of high As groundwater in the Ganges delta. In comparison, less investigation has been carried out on high As groundwater (>50 \(\mu\)g L\(^{-1}\)) in the northwest of China, where geological, hydrogeological and climate conditions are quite different than the Ganges delta. In the northwest of China, high As groundwater mainly occurs in Upper Pleistocene alluvial and lacustrine aquifers with the water type of Na-Cl-\(\text{HCO}_3\) within an arid/semiarid continental climate (Guo and Wang, 2005; Guo et al., 2008a), while that in Holocene alluvial-lacustrine deposits with the water type of Ca-(Mg)-\(\text{HCO}_3\) within a humid tropical climate in the Ganges delta (McArthur et al., 2004; Itai et al., 2008; Mukherjee et al., 2009). The Hetao basin is a typical sediment-filled basin in the northwest of China, where high As groundwaters were first reported in 1994. Aquifer sediments are mainly composed of silt, silty sand and fine sand. Due to gentle surface topography and low hydraulic conductivity of the aquifer sediments, groundwater is mostly stagnant (Guo et al., 2008a). However, shallow groundwater flow system has been substantially affected by irrigation channels and drainage channels. Irrigation with water from the Yellow River was initiated in Qin Dynasty, and this system has been updated since 1958, including the main irrigation channel with a length of 179 km and water flux of 565 m\(^3\) s\(^{-1}\), and the secondary channels with a total length of 800 km. The main and secondary drainage channels have been utilized to locally lower the groundwater table and reduce groundwater evaporation discharge for the purpose of land salinity remediation since 1965. The main drainage channel has a length of 260 km and water flux of 30 m\(^3\) s\(^{-1}\), while the secondary
have a total length of 740 km. Accordingly, these water ways would substantially change shallow groundwater geochemistry as well as natural hydrogeochemical processes.

Our previous studies showed that high As groundwaters generally (>50 μg L⁻¹) occur in the shallow alluvial-lacustrine aquifers in reducing conditions and groundwater As is believed to originate from exchangeable As and Fe-Mn oxide-binding As in the aquifer sediments from the Hetao basin (Guo et al., 2008a). Incubation of intact aquifer sediments confirmed that As is released from Fe/Mn oxides in suspensions of the sediments amended with glucose as organic carbon (Guo et al., 2008b). However, no studies have focused on the effects of the water ways on groundwater chemistry and geochemical processes. Moreover, high As groundwater usually have high dissolved organic carbon (DOC) concentrations in reducing conditions. Although incubation experiments showed that As release is closely related to microbially mediated mobilization of the sediment As (Guo et al., 2008b), evidences of biogeochemical processes remain to be revealed in terms of isotope characteristics of groundwater systems. The investigation on hydrogeogetic and biogeochemical effects on As distribution provides insight into mechanisms of As mobilization in shallow groundwater systems.

The objectives of this study are to 1) characterize groundwater chemistry in different areas; 2) evaluate hydrogeological/hydrochemical controls of As distribution; 3) assess importance of biogeochemical constraints in As mobilization; and 4) provide information for target aquifers as safety drinking water resources.

2. Hydrogeological settings

The basin is located between the Yellow River to the south and the Langshan Mountains to the north. The Langshan Mountains are mainly composed of a metamorphic complex (slate, gneiss and marble), generally of Jurassic to Cretaceous age. As one of the Cenozoic rift basins, the basin is fault-bounded. Aquifer sediments are mainly composed of alluvial-pluvial sand, sandy silt, lacustrine and fluvial-lacustrine sandy silt, silty clay and clay rich in organic matter in the central part of the basin, fluvial sand-fine sand on river banks, and alluvial sand in fan areas. More details are provided by Guo et al. (2008a). The radiocarbon age of the aquifer sediments at 23 m depth is about 23.0 ka conventional radiocarbon years before present (BP), and at a depth of 9 m 12.0 ka BP (unpublished data), which indicates that the high As aquifer sediments were deposited in the late Pleistocene. Due to the gentle land surface, groundwater is mostly stagnant. However, shallow groundwater flow systems have locally been affected by irrigation channels and drainage channels (Fig. 1).

3. Sampling and analysis

Eighty water samples were collected in July 2009 across the basin, including 75 groundwater samples, 2 irrigation water samples, 2 drainage water samples and 1 rainwater sample (Fig. 1). Parameters, including water temperature, Ec, pH, Eh, H₂S, Fe(II), NH₄⁻–N, and alkalinity were measured at the time of groundwater sampling. Water samples were also collected for subsequent laboratory analysis. More details have been provided in Text T1 of Supplementary Material.

4. Results

4.1. General groundwater chemistry

Groundwater pH is near-neutral to weakly alkaline (7.14–8.95). Electronic conductivity ranges between 481 and 9500 μs cm⁻¹. Sodium is the predominant cation, mostly varying from 130 to 2050 mg L⁻¹ (Table S1 in Supplementary Material). The ranges of Cl⁻ and HCO₃⁻ concentrations are 30.7–2510 mg L⁻¹, and 191–1450 mg L⁻¹, respectively. The groundwaters are mainly of Na–Cl–HCO₃ type.

Concentration of DOC is relatively high, ranging from 2.65 to 71.7 mg L⁻¹ (median 12.1 mg L⁻¹). Redox potentials range between −193 and 87.0 mV (median −118 mV), showing moderate reducing conditions of the aquifers. Concentration of NO₃⁻ is mostly below detection limit (<0.01 mg L⁻¹) (median 1.04 mg L⁻¹). Groundwaters generally contain high concentrations of NO₂⁻ and NH₄⁺, with the ranges of <0.01–6.29 mg L⁻¹, 0.1–12.5 mg L⁻¹, respectively. Hydrogen sulfide was detected in most samples, ranging from <1.0 to 40 μg L⁻¹ (Table S1 in Supplementary Material).

Redox-sensitive elements were detected, concentrations of which are dependent on redox conditions. Under anoxic conditions, concentrations of total Fe (Fe₅₇) and Mn are mostly high, ranging 0.01–5.10 mg L⁻¹ and 1.0–996 μg L⁻¹, respectively, which are lower than those in high As groundwaters from Bangladesh and West Bengal (<0.03–29.2 mg L⁻¹ and 0.12–2.03 mg L⁻¹, respectively) (Nickson et al., 2000). Ferrous ion concentration ranges between <0.01 and 2.73 mg L⁻¹. The ratio of Fe(II) to Fe₅₇ is up to 1.00 (Table S1 in Supplementary Material). In contrast, concentrations of U and Mo are generally less than 5.0 and 8.0 μg L⁻¹, respectively, since U readily precipitates as UO₂ and Mo is insoluble.

Fig. 1. Water ways (including irrigation channels and drainage channels) and location of sampling sites in the study area.
as MoO$_x$ or MoO$_x$S$_{2-x}$ in reducing groundwaters (Tossell, 2005; Moon et al., 2009).

4.2. Arsenic species

Arsenic concentrations range between 0.33 and 857 $\mu$g L$^{-1}$ (Table S1 in Supplementary Material). High As groundwaters have relatively low Eh values ($< -100$ mV) (Fig. 2a). Eh values of groundwaters from moderate flow-reducing area and low flow-reducing area are generally lower than those from discharge-evaporation area. Inorganic As(III) concentrations are variable, ranging between $<1.0$ and 755 $\mu$g L$^{-1}$ (median 32 $\mu$g L$^{-1}$). Of the analyzed samples, 77.3% have ratios of inorganic As(III) to total As greater than 65%. The As(III)/As(V) ratios are generally higher in groundwaters with lower Eh values (Fig. 2b). In the discharge-evaporation area, groundwaters generally have lower ratios of As (III) to total As in comparison with other areas. Although DOC concentrations are high (median 12.1 mg L$^{-1}$), organic As compounds were not detected (MMA and DMA $< 2 \mu$g L$^{-1}$). Gong et al. (2006), Guo et al. (2008a) and Deng et al. (2009) also did not detect methyl arsenicals in the Hetao groundwaters.

4.3. Isotopes

Results show that $\delta^{18}$O and $\delta$D values vary from $-4.20^{\circ}_{\text{an}}$ to $-12.1^{\circ}_{\text{an}}$, $-47.7^{\circ}_{\text{an}}$ to $-92.8^{\circ}_{\text{an}}$, respectively (Table S1 in Supplementary Material). All samples are located around or deviate to the right of the local meteoric water line (LMWL) (Yang et al., 2009) (Fig. 2c), indicating their meteoric origin and the effect of evapotranspiration. The groundwaters from moderate flow-reducing area and low flow-reducing area have similar $^{18}$O and $D$ compositions with rainwater and irrigation water. This indicates that the shallow groundwater is the result of mixing of rainwater and irrigation water (Sengupta et al., 2008). However, $^{18}$O and $D$ compositions of groundwaters from discharge-evaporation areas are identical to those of drainage water. The groundwater samples are more enriched in $^{18}$O and $D$ in comparison with the neighboring Huhholt groundwater (from $-9.4^{\circ}_{\text{an}}$ to $-13^{\circ}_{\text{an}}$, $-68^{\circ}_{\text{an}}$ to $-99^{\circ}_{\text{an}}$, respectively) (Smedley et al., 2003).

Forty four samples have been analyzed for the isotopic composition of the S in dissolved SO$_4^{2-}$ (Table S1 in Supplementary Material). The $\delta^{34}$S values of groundwater samples range between $+6.0^{\circ}_{\text{an}}$ and $+39.7^{\circ}_{\text{an}}$ CDT, while SO$_4^{2-}$ in the irrigation water has a much lower $\delta^{34}$S value ($+5.43^{\circ}_{\text{an}}$), indicating a possible origin from SO$_4^{2-}$ reduction in the groundwater. The bacteria-mediated reduction process should preferentially remove the lighter isotope $^{32}$S and result in $^{34}$S enrichment of the residual SO$_4^{2-}$ (Clark and Fritz, 1997). In comparison with the neighboring Huhholt groundwater ($\delta^{34}$S between $-3.8^{\circ}_{\text{an}}$ and $+16.9^{\circ}_{\text{an}}$), the Hetao groundwaters are more enriched in $^{34}$S isotope.

5. Discussion

5.1. Hydrogeochemical zonation

High As concentrations were mainly observed in groundwaters with Na$^+$ as the predominant cation and HCO$_3$ as the major anion (Fig. S1 in Supplementary Material). Groundwaters in stagnant areas contain both high As ($>50$ mg L$^{-1}$) and SO$_4^{2-}$ ($>200$ mg L$^{-1}$) concentrations, which generally occur in the center of palaeo-lakes. Relatively low As ($0.37$–$104$ mg L$^{-1}$, median $34.0$ mg L$^{-1}$) and high TDS ($966$–$4750$ mg L$^{-1}$, median $1360$ mg L$^{-1}$) were found in groundwaters near the drainage channels.

Although geological and hydrogeological conditions are irregular at a local scale, the general hydrogeochemical zonation helps to explain the chemical distribution of the groundwater and delineate the geochemical processes in the aquifers. Arsenic concentrations and the major geochemical and isotopic features, in relation to the spatial distribution of the samples, permit recognition of the following hydrogeochemical zones with distinct characteristics.

5.1.1. Zone I

Groundwater moderate flow-reducing zone. This zone is mainly located in recharge and intermediate areas (Fig. 1), including alluvial fans, overflow areas in front of the fans and irrigation channel-affected areas. The topography gradient lies in the range of 1/100 and 1/5000, and the hydraulic conductivity ranges between 10–20 m/d (Inner Mongolia Institute of Hydrogeology, 1982). Arsenic concentrations range between 0.002 and 0.2 mg/L. Arsenic concentrations range between 0.33 and 857 mg L$^{-1}$ (median 30.6 mg L$^{-1}$) with a wide range of Eh values (Fig. 2a). The ranges of Cl$^-$, SO$_4^{2-}$ and HCO$_3$ concentrations are $30.7$–$1580$ mg L$^{-1}$, $<0.2$–$923$ mg L$^{-1}$, and $191$–$1150$ mg L$^{-1}$, respectively. Sodium concentration falls in the range 29.8–$1160$ mg L$^{-1}$. Hydrogen sulfide concentrations lie between $<1.0$ and $34.0$ mg L$^{-1}$. The $\delta^{34}$SO$_4$ values vary from $+6.00^{\circ}_{\text{an}}$ to $39.7^{\circ}_{\text{an}}$.

High As groundwaters mostly contain quite low NO$_3$ concentrations (mostly $<5.0$ mg L$^{-1}$) and SO$_4^{2-}$ ($<100$ mg L$^{-1}$) (Fig. 3d), indicating that reducing conditions are the major factor controlling As concentration. There is a good correlation between SO$_4^{2-}$ and HCO$_3$ in low As groundwaters ($<50$ mg L$^{-1}$) (Fig. 3c). Furthermore, the samples containing As concentrations greater than $200$ mg L$^{-1}$ generally have the pH $>8.3$, indicating that desorption of As in high pH could be another cause for the As mobilization. Although high

![Fig. 2. Variation of total As with Eh (a), As(III)/As(V) with Eh (b), and stable $^{18}$O with $^2$H compositions (c) of water samples from the Hetao basin. Data of Yellow River water are from Yuan et al. (2006).](image-url)
Fig. 3. Variation of $\text{SO}_4^{2-}$ with $\text{Cl}^-$ (a), Na with $\text{Cl}^-$ (b), $\text{HCO}_3^-$ with $\text{SO}_4^{2-}$ (c), $\text{NO}_3^-$ with $\text{SO}_4^{2-}$ (d), $S_{\text{ siderite}}$ with Fe(II) (e) and $\text{HCO}_3^-$ (f), $S_{\text{ pyrite}}$ with Fe(II) (g) and $H_2S$ (h) in groundwaters with different As concentrations.
Na⁺ waters have high Cl⁻ concentrations (>400 mg L⁻¹), they do not contain high As concentrations (>50 µg L⁻¹) (Fig. 3b). This indicates that As enrichment is independent on evaporation. Groundwaters with Fe(II) > 0.25 mg L⁻¹ and As > 200 µg L⁻¹ are mostly oversaturated with respect to siderite (Fig. 3e). Although siderite has capacity to remove As from water (Guo et al., 2007), As readsorption or coprecipitation on/with siderite seems to have less effect on As diminishing in the waters. Additionally, all groundwaters are oversaturated with respect to pyrite (Fig. 3g and h).

5.1.2. Zone II

Groundwater low flow-reducing zone. This zone is mainly located in the centre of palaeo-lake sedimentation with topography gradient between 1/5000 and 1/8000, and hydraulic conductivity between 2.2–10 m/d (Inner Mongolia Institute of Hydrogeology, 1982). The groundwater flow rate ranges between 0.0003 and 0.002 m/d (Fig. 1). Arsenic concentrations range 53.3–440 µg L⁻¹ (median 131 µg L⁻¹). Concentrations of Cl⁻, SO₄²⁻ and HCO₃⁻ are little higher than those from zone I (Fig. 3). Concentrations of Fe(II) and H₂S are the highest (median 1.28 mg L⁻¹ and 10 µg L⁻¹, respectively). High SO₄²⁻ concentration (236–1170 mg L⁻¹) possibly originates from the leaching of sulfate minerals in the lacustrine sediment, where mirabilite was found in the silty clay. The δ¹⁸O values vary from +10.9‰ to −22.1‰, which is similar to those in zone I. Although the groundwater occurs in reducing conditions, the median of NO₃⁻ concentration is a little higher than that in Zone I. Since zone II waters are mainly located in the agricultural areas, NO₃⁻ likely originates from agricultural activities. Similar to zone I, groundwater samples contained As concentration > 200 µg L⁻¹ mostly have the pH greater than 8.0.

There are good correlations between SO₄²⁻ and Cl⁻, Na⁺ and Cl⁻ (Fig. 3a and b). High TDS (610–3580 mg L⁻¹) groundwaters generally contain high As (53.3–440 µg L⁻¹), indicating that evaporation is a likely cause for the elevated As concentrations. High Fe(II) and HCO₃⁻ concentrations cause the over-saturation of siderite in the waters (Fig. 3e and f). It seems that As concentrations are less affected by precipitation of Fe minerals (including siderite and pyrite) (Fig. 3e and g). Both evaporation and reducing conditions would enhance As enrichment in the waters.

5.1.3. Zone III

Groundwater discharge-evaporation zone. This zone is located close to the groundwater drainage channels (Fig. 1), where groundwater is locally discharged. Due to the impact of surface water in the channels, groundwater Eh is generally high (−144–32 mV, median −85 mV), while groundwater As is relatively low (0.37–103 µg L⁻¹, median 34.0 µg L⁻¹) (Fig. 2a). The low As concentration is likely linked to the presence of more oxic condition in this zone, and hence preferential adsorption of As on the aquifer sediments. Concentration of H₂S is the lowest, and concentrations of Cl⁻, SO₄²⁻ and Na⁺ are the highest because of strong evaporation (Fig. 3). Accordingly, electric conductivity is very high with the range of 1930–9500 µS cm⁻¹ (median 2680 µS cm⁻¹).

5.2. Impact of drainage/irrigation channels on As distribution

Drainage channels have been used to discharge groundwater for the purpose of locally lowering groundwater tables in the evaporation-discharge area (zone III). They have enhanced local groundwater flow rate. Groundwater chemistry in the zone, especially As, is distinct from others, implying that drainage channels would locally affect groundwater geochemistry. Five water samples, located in different distances from the main drainage channel (340–3170 m), were selected for evaluating the effect of the drainage channel on groundwater As. Variations of Eh, H₂S, total As and As(III) are indicated in Fig. 1).
concentrations with the distance are shown in Fig. 4a. Near the drainage, As concentrations are significantly lower than those in the distance > 1.0 km. Coincidently, concentration of H2S exhibits the same trend. However, Eh value shows the opposite trend. Therefore, the low As concentration (<50 μg L⁻¹) near drainage channels is associated withoxic conditions. The fluctuation of channel water table leads to intensive interaction between the surface water and the shallow groundwater, resulting in a pulse of oxygen-rich water that likely recharges the groundwater (Wells 2 and 3 in Fig. 5). Furthermore, the drainage channels enhance the flow rate of local groundwater, which promotes groundwater flushing and removal of As in the channel-affected regions (Stute et al., 2007). However, a quite high As concentration (433 μg L⁻¹) was observed in well 39 (with a screening depth of 100 m) near the drainage channel (about 710 m), suggesting that the drainage channel has less effect on the chemistry of deep groundwater (Well 1 in Fig. 5). Therefore, the channel-affected region is dependent on hydrogeological setting. More investigation needs to be carried out to reveal roles of local geological conditions, the depth of the channel, and the water table in the channel on the dimension of the zone.

In addition, water in the irrigation channel locally recharges shallow groundwater. It was observed that groundwater Eh increases with decreasing distance away from the irrigation channel, and concentrations of total As and As(III) decrease (Fig. 4b). Near the channel, As concentrations are much lower than those in the distance > 2.0 km. This implies that the irrigation channels affect groundwater quality more intensively than the drainage channels. The reason is that the water table in the irrigation channel is usually higher than local groundwater table, which leads to the continuously recharge of oxygen-rich water into the aquifers near the channels (Fig. 5). The more oxic conditions, resulting from the recharge, cause preferential adsorption of As onto the sediments. Métal et al. (2008) also showed that surface water recharge appears to play a particularly important role through dilution with As-depleted water and an associated input of electron acceptors that favors adsorption of As. Concentration of H2S generally exhibits the same trend as As, although Fe(II) would precipitate with H2S as pyrite.

In the study area, DOC concentration of the drainage water (7.26 mg L⁻¹) is lower than those of groundwaters (11.9–40.8 mg L⁻¹). It seems that migration of DOC from the drainage water would not increase groundwater DOC concentration and therefore promote As release. Downward migration of DOC-enriched groundwater originating from surface water bodies was reported in Bangladesh by Harvey et al. (2002), which was expected to be responsible for As mobilization (Rao et al., 2009; Nagar et al., 2010; Poya and Charlet, 2009). In contrast, Kim et al. (2009) showed that the supply of NO₃⁻ and SO₄²⁻ from land surface limited As concentration of shallow groundwater at the rice cultivation sites with good permeability of surface sediments.

Although groundwaters have low As concentrations near the drainage channels, they contain much high TDS values (mostly > 1500 mg L⁻¹). Therefore, target aquifers for safe drinking water resources are expected to be available near the irrigation channels.

5.3. Hydrogeological control on As mobilization

A hydrogeologic unit was selected for investigating the hydrogeological control on As mobilization around a typical alluvial fan of the study area. Subsurface geology is relatively simple, as described by Guo et al. (2010).

Redox potential ranges from –156 to 870 mV. In general, Eh exhibits higher values in the recharge zone than from further down-gradient along the flow path, with exception of well 69 having a screening depth of 100 m (Figs. 1 and 4c). Groundwaters exhibit a progressive decrease in redox potentials as evidenced by Eh value, H2S, and Fe(II) concentrations (Fig. 4c). Arsenic concentration increases with the decrease in Eh value, since it is readily mobilized in anaerobic aquifers (Smedley and Kinniburgh, 2002; Kim et al., 2009; Chauhan et al., 2009). Although groundwater samples are mostly over-saturated with respect to pyrite and siderite, which is believed to scavenge As from waters (Guo et al., 2007), As concentration increases along the groundwater flow path. Results show that low As groundwater (≤50 μg L⁻¹) is presented in alluvial fans, which can also be served as safe drinking water resources.

5.4. Importance of microbial processes in As release

Because of the conservative behavior of Cl⁻, decreasing SO₄²⁻/Cl⁻ ratios indicates removal of SO₄²⁻ from the water (Berner et al., 2002). Sulfate concentrations were normalized to Cl⁻ concentrations in order to evaluate the effect of net changes in SO₄²⁻/Cl⁻ concentration on S isotopic composition. Ratios of SO₄²⁻ show a negative correlation with δ³⁴S values in groundwaters from zones I and II (Fig. 6). This correlation suggests that bacterial reduction of SO₄²⁻ occurs in the aquifers from these zones. In contrast, there is a poor correlation between SO₄²⁻/Cl⁻ ratio and δ³⁴S value in groundwaters from zone III. The likely reason is that reoxidation of sulfide occurs and alters the isotopic composition of dissolved SO₄²⁻.

Incubation of intact sediments from the Hetao aquifers shows that SO₄²⁻ reduction occurred in the glucose-amended suspension with the reduction rate of approximately 0.079 mg SO₄²⁻ per day (unpublished data). Sulfate reduction bacteria (SRB) were also detected in intact aquifer sediments (Guo et al., 2008b). This confirms that microbial reduction of SO₄²⁻ has taken place in the Hetao aquifers.

In the glucose-amended suspension of the Hetao intact aquifer sediment, the increase in As concentration is well correlated with the decrease in SO₄²⁻ concentration (Fig. S2 in Supplementary Material). This indicates that As is mobilized under the reducing conditions along with the reduction of SO₄²⁻. SRB, such as Desulfotomaculum auripigmentum strain OREX-4 (Newman et al., 1997), would simultaneously reduce SO₄²⁻ and As(V), which result in a release of more mobile As(III).

However, there is a little overall correlation between δ³⁴S value and As concentration in the studied groundwaters (Fig. S3 in Supplementary Material). The possible reason is that in addition to SRB, both nitrate reducers and Fe(III) reducers would mediate As
Additionally, Fe/Mn oxide reduction is occurring or has occurred prior to SO$_4^{2-}$ reduction (Mukherjee et al., 2009). Our data also show that reduction of Fe oxide minerals is an active hydrogeochemical process in the aquifer due to the high concentrations of Fe (>0.5 mg L$^{-1}$). Arsenic would be released by means of reductive dissolution of Fe/Mn oxyhydroxides and reductive desorption of As from those minerals in the reducing conditions, which are proposed to be the major mechanisms for As mobilization in the Bengal delta sediments (Islam et al., 2004). Therefore, microbe-related biogeochemical processes play an important role in As mobilization in the aquifers of the Hetao basin.

6. Conclusion

D and $^{18}$O isotope geochemical studies indicate that shallow groundwaters of the Hetao basin is originated from the meteoric water, although they are affected by the evaporation. The major geochemical and isotopic features in relation to the spatial distribution of the samples permit recognition of three hydrogeochemical zones with distinct characteristics, including groundwater moderate flow-reducing zone (zone I), groundwater low flow-reducing zone (zone II), and groundwater discharge-evaporation zone (zone III). Zone I is mainly located in recharge and intermediate areas, including alluvial fans, overflow area in front of the fans, and irrigation channel-affected areas, where As concentration is generally dependent on reducing conditions, instead of groundwater evaporation. Evaporation seems to increase As concentration in the zone II. Suboxic-weakly reducing conditions were observed in the zone III. This zone is close to the groundwater drainage channels, where the exchange between groundwater and surface water is moderately intensive and As concentrations are the lowest. Groundwater Eh increases with decreasing distance away from the irrigation/drainage channels, and concentrations of total As and As(III) decrease. This study demonstrates that both the drainage channels and the irrigation channels change natural hydrogeological settings, especially causing oxygen-rich water to recharge the groundwater and remove As, although more detailed studies are required to determine the extent. In the selected hydrogeological unit, As concentrations increase with a progressive decrease in redox conditions from the recharge area to the discharge area. A negative correlation between SO$_4^{2-}$/Cl$^{-}$ ratios and the $^{34}$S values of SO$_4^{2-}$ indicates that the bacterially reduction of SO$_4^{2-}$ has occurred in reducing groundwaters. Although incubation study shows that As is mobilized under the reducing conditions along with the reduction of SO$_4^{2-}$ in the presence of indigenous bacteria and the organic nutrient as an electron donor, a little overall correlation was found between $^{34}$S value and As concentration. Reductive dissolution of Fe/Mn oxides, occurs prior to SO$_4^{2-}$ reduction, and is believed to cause As release from the aquifers. Therefore, microbe-related biogeochemical processes may play an important role in As mobilization in the aquifers of the Hetao basin.

Acknowledgement

The study has been financially supported by National Natural Science Foundation of China (No. 40872160), the Program for New Century Excellent Talents in University (No. NCET-07-0770), and the Chinese Universities Scientific Fund (No. 2010ZD04). We appreciate Kirk Nordstrom, U.S. Geological Survey, for helpful comments on earlier drafts of this manuscript. Constructive comments by the editor, Philip Verplanck and other anonymous reviewers are also gratefully acknowledged.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2010.12.029.

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