

Role of colloidal particles for hydrogeochemistry in As-affected aquifers of the Hetao Basin, Inner Mongolia

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(Received August 14, 2008; Accepted January 9, 2009)

High As groundwater was found in shallow aquifers of the Hetao Basin, Inner Mongolia, which has caused serious chronic arsenism. Groundwater particles are ubiquitous in natural aquifers, and significantly affect As mobilization and transportation. This study has investigated their effect on element hydrogeochemistry. Groundwater samples were filtered in the field through a progressively decreasing pore size (10, 5, 3, 1, 0.8, 0.45 μm). Unfiltered samples were also taken. Chemical analysis of 43 groundwater samples shows concentrations of most elements (Ba, Co, Mn, Mo, Ni, V, Sr, Mg, Ca, Na, K) in unfiltered samples are well correlated with those in <0.45 μm fraction, and the ratios between them are close to 1.00. Those elements are considered to be present in the form of true dissolved group and are not affected by the filtration. Although saturation indices for calcite and dolomite are greater than 0, they could possibly exist as small size colloids (<0.45 μm) in groundwater. Concentrations of Cd, Pb, Fe, and Al in <0.45 μm fraction are mostly less than those in unfiltered fraction, implying that large-size inorganic-rich (Al/Fe complexing) colloids could be possible carrier for Cd and Pb in the groundwaters. Arsenic, Cu, Zn and Cr are fallen into another group. These elements could mainly be associated with organic-complexing colloids with particle size less than 0.45 μm , although As could partially be carried by large-size colloids. In groundwaters saturated with respect to pyrite and siderite, a small proportion of As (about 15%) is associated with large-size Fe complexing particles (>0.45 μm). Larger amounts of As is trapped with small size organic colloids, which has been confirmed by the ultrafiltration. The study suggests that groundwater particles transported in the aquifers could affect element geochemistry, especially for As expected to be associated in small size complexes.

Keywords: aqueous geochemistry, arsenic, colloid, shallow groundwater

INTRODUCTION

Because of the small size, colloid particles tend not to settle out of suspensions, being influenced by Brownian motion and minor currents in the bulk solution (Stumm and Morgan, 1996). Among the most important processes affecting the geochemical cycles of trace elements, are the physiochemical transformations of colloid particles that occur in the aquifers (Boyle *et al.*, 1974). Colloids may adsorb trace metal ions and waterborne pollutants, thus possibly governing, via their movements in aqueous systems, the fates of reactive elements and/or pollutants (Pourret *et al.*, 2007).

Recent studies have shown that high As groundwater mostly occurs in Quaternary alluvial (alluvial-lacustrine) and deltaic plains, including the Datong Basin, the Hetao

Basin, the Huhhot Basin, the Bengal Basin, Mekong and Red River Deltas and elsewhere (Guo *et al.*, 2003; Smedley *et al.*, 2003, Berg *et al.*, 2007; Guo *et al.*, 2008). One feature of particular interest is the relatively high concentration of dissolved organic matter in some As-rich groundwater (McArthur *et al.*, 2004; Guo *et al.*, 2008). Groundwaters in shallow aquifers from the Hetao Basin are mostly discoloured and frothy, possibly indicating that inorganic and/or organic colloids are widely present. However, there is a lack of information on role of groundwater particles on element distribution and its implication for particle hydrogeochemistry in As-affected aquifers.

Considering that the respective contribution of groundwater particles to As mobilization remains unsolved, this work is dedicated to (i) investigating effect of colloid particles on element concentrations of groundwater in the Hetao aquifers, and (ii) providing new insights into the hydrogeochemical behavior and status of trace elements (especially As) in As-affected aquifers.

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MATERIALS AND METHODS

Study area

The Hetao Basin is located in the western part of Inner Mongolia, on the northern margins of the Yellow River, and on the eastern fringe of the Wuranbuh Desert. It is one of the Cenozoic rift basins with elevation varying between around 1060 and 1007 m. Due to the complex tectonic movement and sedimentation environment, the sediments are heterogeneous both spatially and with depth (Guo *et al.*, 2008). The shallow aquifers can be subdivided into alluvial-pluvial unconfined aquifers and alluvial-lacustrine leaky-confined aquifers. High As groundwaters are mainly present at the transition zone between alluvial-pluvial aquifers and alluvial-lacustrine aquifers, and in alluvial-lacustrine aquifers. Geological and hydrogeochemical settings of the area have been described in more details by Guo *et al.* (2008).

High As groundwaters are found in shallow aquifers from the Hetao Basin of Inner Mongolia. Arsenic concentrations range between 0.6 and 572 $\mu\text{g/L}$, with 71% of the selected samples exceeding the Chinese Drinking Water Standard of 10 $\mu\text{g/L}$. They are characterized by high concentrations of dissolved Fe, Mn, HCO_3^- , and S^{2-} , and low concentrations of NO_3^- . Redox potentials of groundwaters range from -153 to 83 mV, reflecting the moderate reducing environment of the aquifers. The occurrence of S^{2-} , together with relatively low SO_4^{2-} concentration in the reducing environment, suggests that SO_4^{2-} reduction has taken place. Spatial distribution of groundwater As has been described by Guo *et al.* (2008).

Sample collection

Water samples were collected from hand pump tube-wells across the Hetao Basin. Since the yield of wells is relatively low (3–5 L/min), hand pump could make sure that sampled particles are exclusively pristine. Parameters, including water temperature, pH, Eh, and sulfide, were measured at the time of groundwater sampling. Alkalinity was measured by the Gran titration method on the sampling day.

Filtered and unfiltered water samples were collected in 2006 for laboratory analysis. Although Stumm and Morgan (1996) note the difficulty in using filtration to isolate suspended particles and the challenges with ascribing metal concentrations to those particles, progressively filtration could provide an effective method to study geochemical behavior of trace elements associated with iron- or organic-rich particles (Pokrovsky and Schott, 2002; Pourret *et al.*, 2007). Five groundwater samples were filtered in the field in 2007 through a progressively decreasing pore size (10, 5, 3, 1, 0.8, 0.45 μm). These five sampling points include three wells used in 2006 (A, B and D, corresponding to Nos. 42, 56 and 9, respectively,

as reported in Guo *et al.*, 2008) and two new ones (C and E). In order to avoid settlement of large particles (mainly 5–10 μm), groundwater sample was *in-situ* filtered in a very short time (5–10 s). Nitrogen gas (>99.999%) was used for the protect gas to make sure that no oxidation occurs during sampling and progressive filtration. All samples were acidified on site to pH 1 using 6 M HNO_3 . One successive filtration was performed in duplicate. Good reproducibility was observed for major and trace element concentrations. Duplicate is better than 5% for all components.

Arsenic(III) in water samples was separated in the field immediately following filtration with As-speciation cartridges (Metalsoft Center, Highland Park, NJ) (Meng and Wang, 1998; Meng *et al.*, 2002). Samples for anion analysis were left unacidified.

Sample analysis

Concentrations of major cations and trace elements were determined by ICP-AES and ICP-MS, respectively. Unacidified aliquots were analyzed for F^- , Cl^- , NO_3^- , NO_2^- , NH_4^+ , HPO_3^{2-} , SO_4^{2-} by Ion Chromatography with an instrument model DX-120 (Dionex). Concentrations of As and Se were determined by atomic fluorescence spectrometry (AFS) with hydride generation. In most cases, analytical charge imbalances were less than 5%. Dissolved organic matter (DOC) was analyzed by TOC-C (Shimadzu, Hongkong).

RESULTS AND DISCUSSION

Filtered vs. unfiltered samples

On a basis of comparison of filtered samples (<0.45 μm) and unfiltered samples, major and trace elements can be divided into three groups: (i) Group I includes alkalis (Na, K), alkaline earth metals (Ca, Mg, Ba, Sr) as well as Ni, Mo, V, Mn and Co; (ii) Group II contains Cd, Pb, Al and Fe; and (iii) Group III includes Cr, Zn, Cu and As.

(i) Group I: “truly” dissolved behavior

Although the filtration procedure does not allow to differentiate between dissolved and small size colloid (<0.45 μm), elements remaining in 0.45 μm filtrates are considered to be truly dissolved. For most samples, concentrations of alkalis such as Na and K do not change during filtration (Fig. 1A). Alkaline elements are mostly presented in the dissolved pool and behave as “truly” dissolved inorganic species. Pokrovsky and Schott (2002) found that both alkalis and alkaline earth in surface waters are present in the form of true dissolved inorganic species. Concentrations of major and trace alkaline earth (Ca, Mg, Ba and Sr) are not affected by filtration since there is no difference between filtered samples and unfiltered samples (Fig. 1). It shows that they were not trapped by high-molecular weight organic colloids or in-

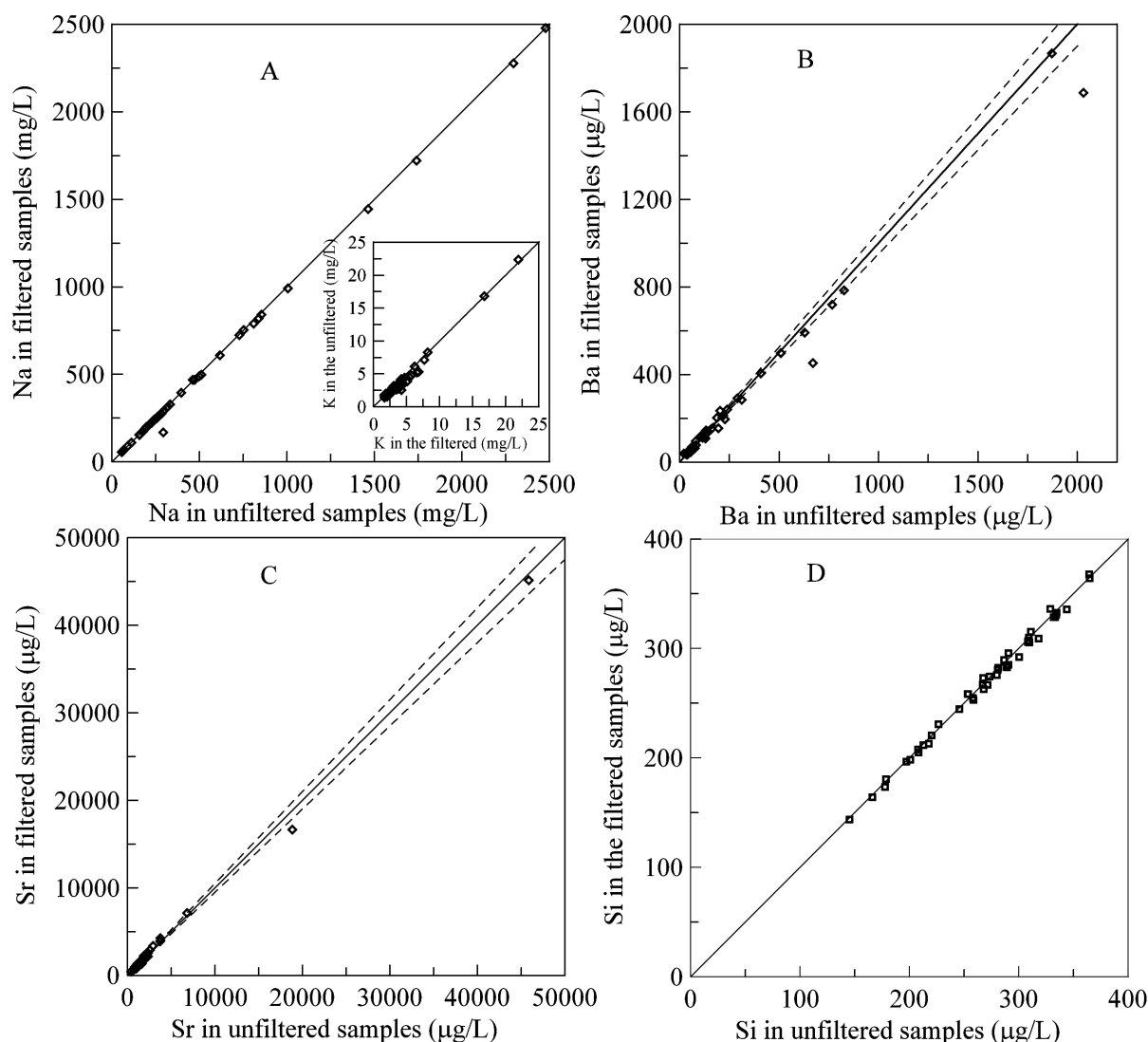


Fig. 1. Comparison of Na, Ba, Sr and Si concentrations in filtered samples and in unfiltered samples. Lower insert in A shows plot of K concentration in filtered samples versus K concentration in unfiltered. Solid lines represent the diagonal; Dashed lines represent a deviation of $\pm 5\%$ from the diagonal.

organic colloids ($>0.45 \mu\text{m}$). However, Shapiro (1964) found that Ca and Mg could be associated with low-molecular weight organic colloid (such as natural fulvic acids). Silicon concentrations displayed no significant variations during the filtration (Fig. 1D), which is believed to occur in a “truly” dissolved state. This suggests that aqueous silica is not trapped by clay mineral or phytolites with the grain size $>0.45 \mu\text{m}$. Concentrations of Ni, Mo, V, Mn and Co do not exhibit large variations through the $0.45 \mu\text{m}$ pore size cut-off, suggesting that the transition metals have to mostly exist as “truly” dissolved species.

(ii) Group II: Al/Fe-complexing (large-size) colloid-associated elements

For most groundwater samples, concentrations of Cd, Pb, Al and Fe in $<0.45 \mu\text{m}$ fraction are mostly less than those in unfiltered fraction, suggesting that those elements do not occur as free species in solution. Two types of colloids can carry these metals (i.e., Al/Fe-rich inorganic colloids or organic-Al/Fe-complexing colloids). Aluminum is observed to be mainly kept in these unfiltered samples, while less is retained in the filtrates (Fig. 2A). Since Si occurs in a “truly” dissolved state, Al may not be presented as clay colloids with the grain size $>0.45 \mu\text{m}$ in groundwaters. Geckeis *et al.* (2003) observed that Al is controlled by Al oxyhydroxides. Therefore, it implies that Al oxyhydroxides and/or Al oxyhydroxide-

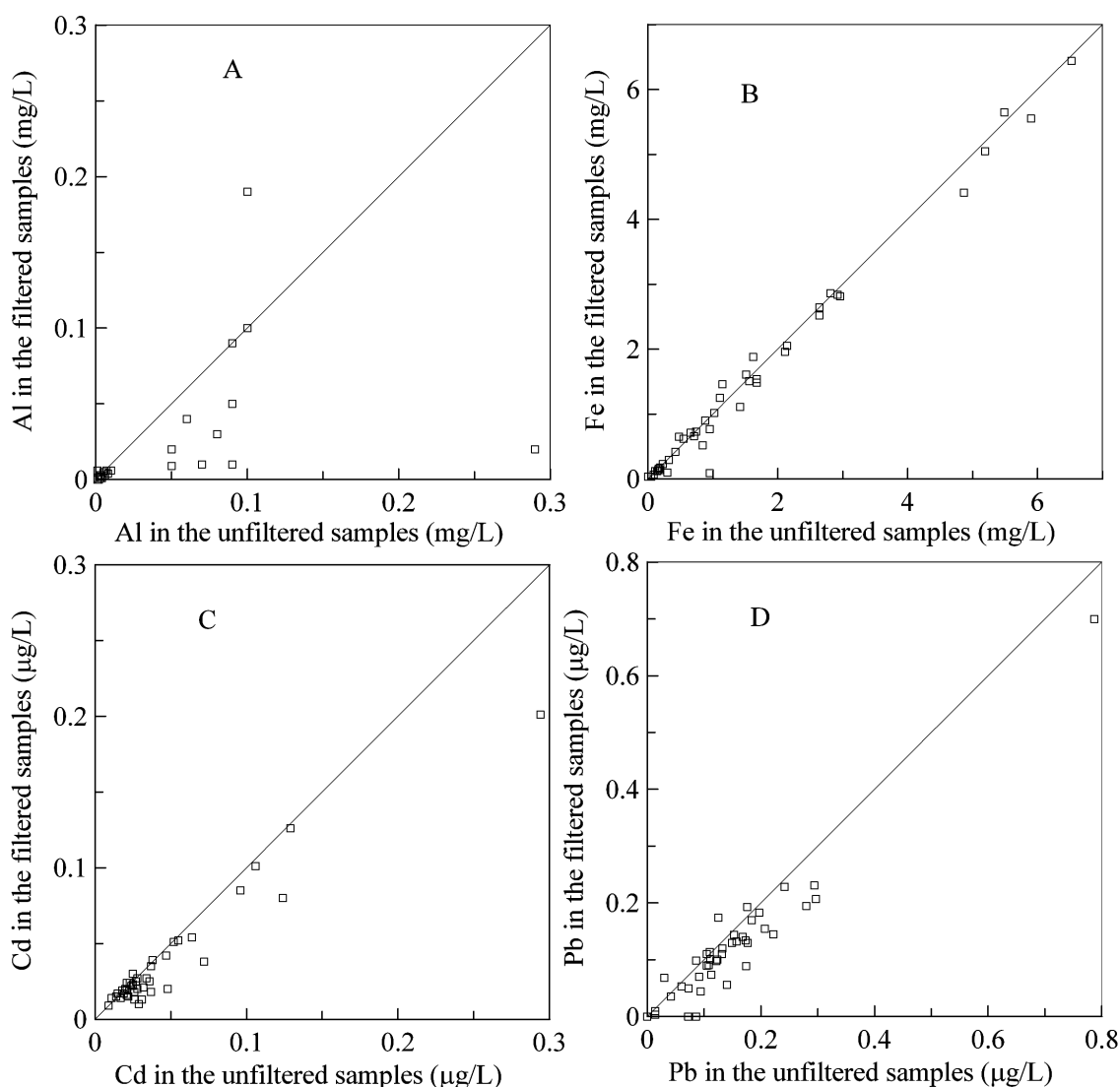


Fig. 2. Comparison of Al, Fe, Cd and Pb concentrations in filtered samples and in unfiltered samples. Solid line represents the diagonal.

organic complexes could be possible carrier for Cd and Pb in the groundwaters (Figs. 2C and D). In addition, large-size Fe-complexing colloids may carry these elements in groundwaters (Fig. 2B), which is discussed later in detail.

(iii) Group III: small-size organic colloid-borne elements

Arsenic, Zn, Cu and Cr are fallen into another group. For most groundwater samples, concentrations of these elements in filtered samples are similar to those in unfiltered samples. Since acidification by 6 M HNO_3 does not decompose dissolved organic matter in groundwater samples, small-size DOC could remain in the filtrates. Iron could form organic-complexing colloids together with small-size dissolved organic matter (Sholkovitz,

1995; Olivié-Lauquet *et al.*, 2000). It suggests that these elements could mainly be associated with organic-complexing colloids with particle size less than $0.45 \mu\text{m}$, although few sampled waters had higher As concentrations in the unfiltered than in the filtered (Fig. 3).

In addition, Zn, Cu and Cr are mainly associated with small-size colloids (data not provided). Xue *et al.* (1995) and Sigg *et al.* (2000) also found that Cu and Zn were strongly bound to larger size colloids, as well as very low molecular weight organic ligands. It was reported that, in Russian boreal rivers, Cr is associated either with small-size ($<10 \text{ kDa}$) organic colloids (r. Pezega and Chernaya) or with Fe colloids (10 kDa – $0.8 \mu\text{m}$), which can contribute up to 50% of dissolved Cr (r. Belukha) (Pokrovsky and Schott, 2002).

Table 1. Saturation indices (SI) for selected minerals in 0.45 μm fractions of five groundwaters

No.	pH	Alkalinity (mg/L)	S^{2-} (mg/L)	SI _{Calcite}	SI _{Dolomite}	SI _{Gypsum}	SI _{Barite}	SI _{Fluorite}	SI _{Siderite}	SI _{Pyrite}
A	7.90	897	0.03	0.39	1.19	-1.82	0.77	-0.79	0.48	13.71
B	8.43	565	0.12	0.83	2.07	-3.51	0.24	-2.42	-0.23	8.54
C	8.80	414	0.08	0.54	2.01	-3.17	0.95	-2.16	0.18	9.96
D	8.04	1193	0.06	0.84	2.42	-4.35	-0.24	-1.42	1.26	12.51
E	8.20	1338	0.13	0.69	2.18	-1.70	0.46	-1.23	1.21	11.93

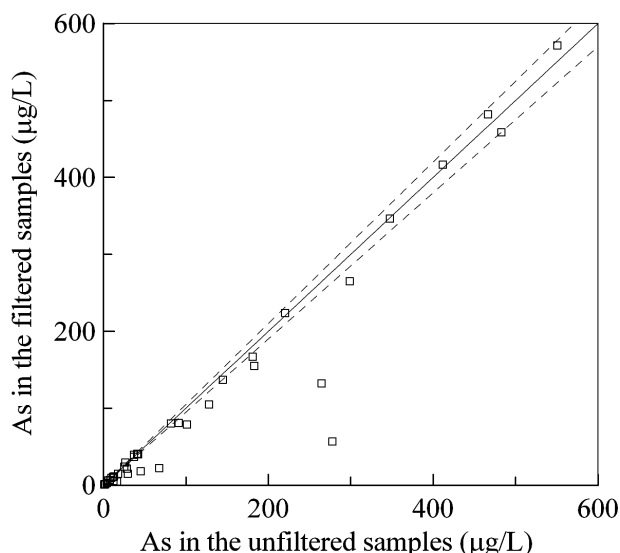


Fig. 3. Comparison of As concentration in filtered samples and in unfiltered samples. Solid line represents the diagonal; Dashed lines represent a deviation of $\pm 5\%$ from the diagonal.

Successively filtered samples

Five groundwaters (including A, B, C, D and E) were successively filtered with filter membranes of pore sizes between 10 and 0.45 μm . As expected, concentrations of all successively filtered samples were equal within measurement error for these “truly” dissolved elements (data not provided).

Saturation indices (SI) for selected minerals were calculated by the hydrogeochemical code PHREEQC (Parkhurst and Appelo, 1999) using MINTEQ database. Results show that these five groundwaters of 0.45 μm fractions are supersaturated with respect to calcite and dolomite (Table 1). Due to the absence of Ca/Mg in the large-size colloid particles, they could be presented as small-size colloids in groundwater samples.

For these large-size colloid-associated elements, their concentrations continuously decrease in successive filtrates through decreasing pore size membranes. Aluminum and Pb vary following the same trend, and are strongly affected by a large drop of concentrations between 10 and

1.0 μm (Figs. 4B and A). In groundwaters, about 60% and 70% for Al and Pb, respectively, are attached to large-size colloid particles with the grain sizes between 1 and 10 μm , except for Sample B with relatively low concentrations of Al and Pb. As mentioned above, these elements could be carried by Al oxyhydroxides.

In addition to Al complexing colloids, Fe species is also present in groundwater solutions as large-size colloid. It can be seen in Fig. 4C that about 30% of Fe exist as large particles between 1 and 10 μm and 60% as colloid between 0.45 and 1 μm in Sample D. In comparison with Fe, less Pd (about 15%) is trapped in the colloid particles between 0.45 and 3 μm in Samples D and E. This suggests that the elements in Group II are mostly associated with large-size Fe complexing colloids. Therefore, a major control of these elements (i.e., Group II, including Pb, Fe, Al, and Cd) is believed to attribute to large-size inorganic-rich (Al/Fe complexing) colloids/particles.

Arsenic concentrations do not exhibit large variations through the different decreasing pore size cut-offs, although a significant decrease in Fe concentration of Samples D and E is observed. A slight drop (about 15%) in As concentration for Sample D occurs between 1.0 and 0.8 μm , and for Sample E between 0.8 and 0.45 μm (Fig. 4D). It speculates that more As appears to be carried by colloids smaller than 0.45 μm . Since about 83% Fe (except for Sample A as 60%) and 70% of Al are removed by the six filtration steps, few colloids could exist as inorganic complexing in <0.45 μm fractions. Iron concentrations in unfiltered samples were a little higher than those in 10 μm filtrates. The portion of Fe being removed by the 10 μm fraction step generally accounts for 10% of total. It can be speculated that a large proportion of As seems to be associated with small size colloids, especially the organic complexes.

Calculation of SI for selected minerals shows that 0.45 μm fractions of Samples D and E are supersaturated with respect to siderite and pyrite (Table 1). Although saturation indices of other fractions (>0.45 μm) can not be calculated since some major compositions (such as HCO_3^- , CO_3^{2-}) have not been determined, it can be speculated that other fractions of Samples D and E are supersatu-

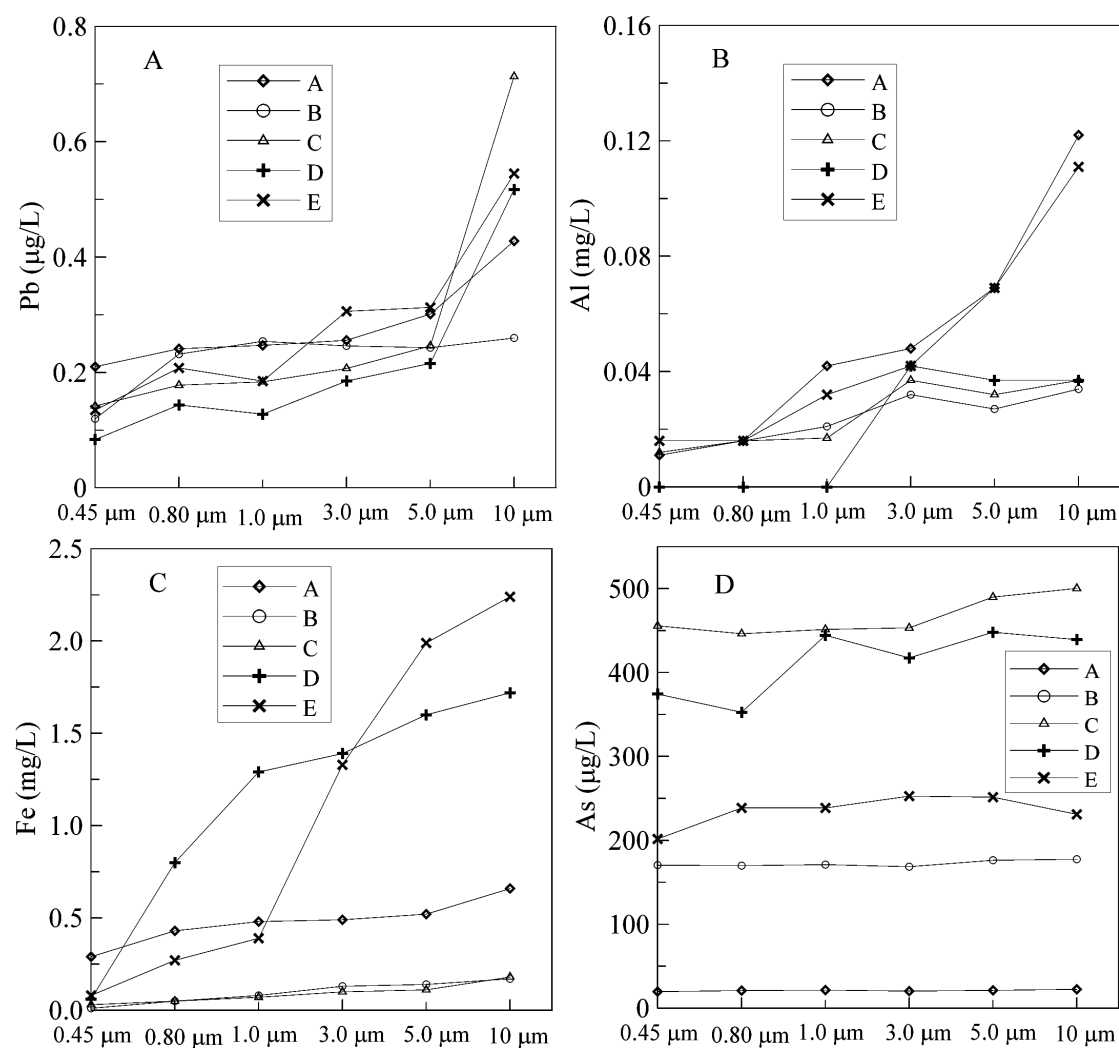


Fig. 4. Variation of Pb, Al, Fe and As concentrations in the successive filtrates from 10 to 0.45 μm .

rated with respect to siderite and pyrite as well. The decrease in Fe concentration during successive filtration could partially result from removal of siderite and pyrite colloids presented in the groundwater samples. Although not examined, the size of siderite and pyrite colloids seems to fall in the range between 0.45 and 10 μm . A small proportion of As could be adsorbed on the surface of the siderite (Guo *et al.*, 2007) and the pyrite (Farquhar *et al.*, 2002). These two colloids could contribute to the slight drop in As concentration during successive filtration.

Implication for groundwater geochemistry

Redox potentials of groundwaters range from -153 to 83 mV, reflecting the moderate reducing environment of the aquifers. The occurrence of S^{2-} in the reducing environment, suggests that SO_4^{2-} reduction has taken place (Guo *et al.*, 2008). In these anaerobic aquifers, Fe^{2+} is

expected to be the dominant Fe species. Since high concentration of Fe is present in groundwater concomitant with the occurrence of S^{2-} , groundwater is supersaturated with respect to pyrite. In addition, most of groundwater tested is saturated with respect to siderite due to $\text{SI}_{\text{siderite}} > 0$. A small proportion of arsenic (about 15%) is proposed to be associated with siderite and pyrite colloids, since they have a good affinity for aqueous As (Farquhar *et al.*, 2002; Guo *et al.*, 2007). This can also be proved by the simultaneous decreases in concentrations of Fe and As during successive filtration in groundwaters (D and E) with both $\text{SI}_{\text{siderite}}$ and $\text{SI}_{\text{pyrite}} > 0$.

Concentrations of TOC in 0.45 μm fractions are in the range between 0.64 and 87.9 mg/L, with an average of 15.8 mg/L. Humic acid as large molecular weight organic ligands is suggested to be present in these filtered groundwaters by Guo *et al.* (2008). As stated above, a

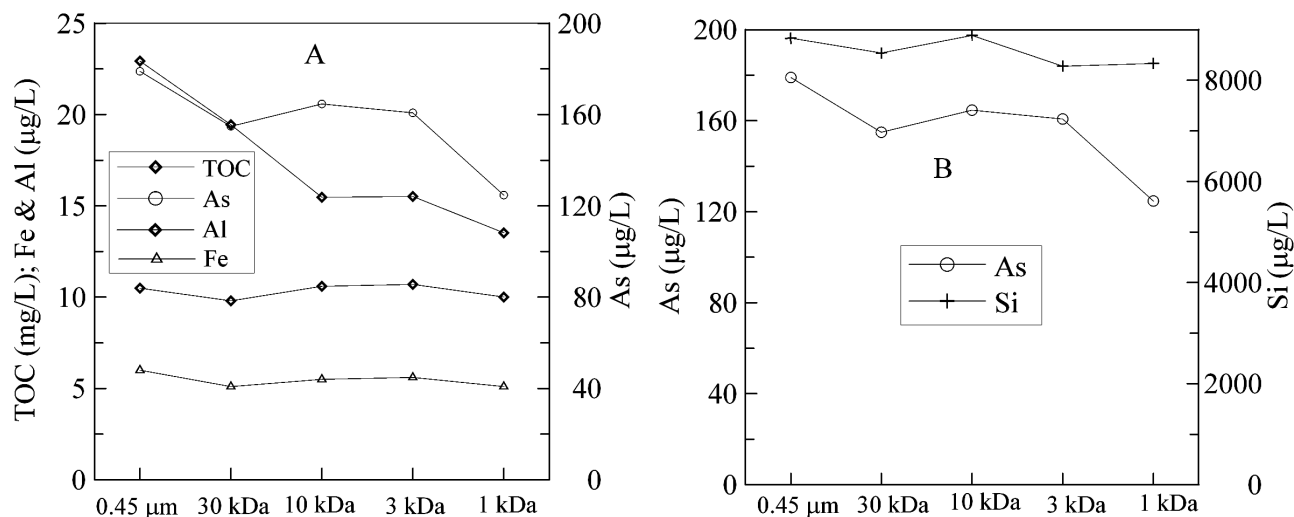


Fig. 5. Variation of TOC, As, Fe, Al and Si concentrations in different filtrates of Sample B during ultrafiltration.

large proportion of As is presumably associated with small size colloids ($<0.45 \mu\text{m}$), especially the organic complexes. This speculation is confirmed by ultrafiltration of groundwater Sample B (Fig. 5). The results demonstrate that As concentrations decreased with the decrease in TOC concentrations. During ultrafiltration with 30, 10, 3 and 1 kDa, about 35% As was retained in the ultrafilters and removed in coincidence with removal of 41% TOC (Fig. 5A), which is much higher than that observed in the laboratory experiments by Buschmann *et al.* (2006). They found that about 10% of total As(V) may be bound to dissolved natural organic matter (DOM), whereas $>10\%$ of As(III) is bound to DOM at very low ratios of As to dissolved organic carbon only.

In contrast, concentrations of Fe and Al in ultrafiltrates kept relatively constant during the successive ultrafiltration (Fig. 5A). Although the correlation coefficient between Fe/Al and As was up to 59%, Fe/Al with low concentrations (mostly $<10 \mu\text{g/L}$) could have less impact on As distribution. In comparison with dissolved organic matter, Fe/Al compositions in groundwater as As carriers could be negligible. Besides, variation of Si concentration lay within the range of measurement error, which is not well-correlated with that of As (Fig. 5B). It suggests that groundwater As was not associated with small size Fe/Al/Si colloids. Therefore, small size organic colloids could be an important host for groundwater As. Due to their small size, As-loading organic complexes are easily transported in the aquifer along with groundwater movement, influencing the fate of As in the groundwater system.

Although about 35% of As is associated with the dissolved organic complexes with molecular weights $>1 \text{ kDa}$ accounting for 41% of TOC, about 50% is distributed in

the $<1 \text{ kDa}$ fraction. This part of As may be dissolved as free oxyanions such as arsenite or arsenate without being associated with organics, and/or be associated with the remaining organic complexes.

CONCLUSION

A filtration was applied to test the role of colloid particles on element concentrations of groundwater in the Hetao aquifers. Comprehensive comparison of element concentrations among 43 filtered samples and 43 unfiltered samples has been made. Three groups of elements are identified with regards to their affinity in different-size colloid particles, which implies consequences regarding related hydrogeochemical processes in the aquifers: (i) a “truly” dissolved behavior group (Na, K, Ca, Mg, Ba, Sr, Ni, Mo, V, Mn and Co), (ii) Al/Fe-complexing (large-size) colloid-associated elements (Cd, Pb, Al and Fe), and (iii) small-size organic colloid-borne elements (As, Zn, Cu and Cr).

Although saturation index for calcite and dolomite are greater than 0, they could not exist in the groundwater as large-size colloid particles, but possibly as small-size colloids. Aluminum is observed to be mainly kept in these unfiltered samples, while less is retained in the filtrates. A larger proportion of Fe, Cd and Pb is trapped in large-size colloid particles. It is evident that a major control of these Group II elements could attribute to large-size inorganic-rich (Al/Fe complexing) colloid particles.

In groundwaters saturated with respect to siderite and pyrite, a small proportion of arsenic (15%) is believed to be associated with large-size Fe complexing particles, since they have a good affinity for aqueous As (Guo *et al.*, 2007). Contrastingly, a large proportion of As is as-

sociated with small size colloids ($<0.45\ \mu\text{m}$), especially the organic complexes, which has been confirmed by the ultrafiltration.

Acknowledgments—This study is financially supported by the National Natural Science Foundation of China (Nos. 40572145, 40872160 and 40710104037), the Program for New Century Excellent Talents in University (No. NCET-07-0770), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education. Constructive comments by associate editor Dr. Yoshio Takahashi and two anonymous reviewers are also gratefully acknowledged.

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