Arsenic in groundwater of the Red River floodplain, Vietnam: Controlling geochemical processes and reactive transport modeling

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Abstract

The mobilization of arsenic (As) to the groundwater was studied in a shallow Holocene aquifer on the Red River floodplain near Hanoi, Vietnam. The groundwater chemistry was investigated in a transect of 100 piezometers. Results show an anoxic aquifer featuring organic carbon decomposition with redox zonation dominated by the reduction of Fe-oxides and methanogenesis. Enhanced P CO2 pressure causes carbonate dissolution to take place but mainly in the soil and unsaturated zone. The concentration of As increases over depth to a concentration of up to 550 g/L. Most As is present as As(III) but some As(V) is always found. Arsenic correlates well with NH4, relating its release to organic matter decomposition and the source of As appears to be the Fe-oxides being reduced. Part of the produced Fe(II) is apparently reprecipitated as siderite containing less As. Results from sediment extraction indicate most As to be related to the Fe-oxide fractions. The measured amount of sorbed As is low. In agreement, speciation calculations for a Fe-oxide surface suggest As(III) to constitute only 3% of the surface sites while the remainder is occupied by carbonate and silica species. The evolution in water chemistry over depth is homogeneous and a reactive transport model was constructed to quantify the geochemical processes along the vertical groundwater flow component. A redox zonation model was constructed using the partial equilibrium approach with organic carbon degradation in the sediment as the only rate controlling parameter. Apart from the upper meter a constant degradation rate of 0.15 C mmol/L/yr could explain the redox zonation throughout the aquifer. Modeling also indicates that the Fe-oxide being reduced is of a stable type like goethite or hematite. Arsenic is contained in the Fe-oxides and is first released during their dissolution. Our model further suggests that part of the released As is adsorbed on the surface of the remaining Fe-oxides and in this way may be retarded.

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1. INTRODUCTION

Groundwater contaminated with arsenic with a concentration exceeding the WHO drinking water limit of 10 µg/L As is a threat to the health of millions of people in Bangladesh and W. Bengal (Yu et al., 2003). A similar predicament has been discovered in the Red River floodplain aquifers, Vietnam, where about 11 million people may be exposed to dangerously high As concentrations (Berg et al., 2001). To remediate the problem of a high As concentration in water supplies based on groundwater it is imperative that the processes leading to the mobilization of As into the groundwater are properly understood. In Bangladesh and W. Bengal, the processes controlling the release of As to the groundwater have been studied intensively but they remain a subject of dispute (see a recent overview in Polizzotto et al., 2006).
In short, there is a consensus among researchers that the As is released from the sediment into the groundwater. All major rivers draining the Himalayas in SE Asia seem to carry sediment containing As, but not in very high concentration (Smedley and Kinniburgh, 2002; Stanger, 2005). However, after sedimentation in flood plains and delta’s, the As may become released to the groundwater. Typically, the Holocene aquifers are anoxic systems dominated by organic carbon degradation coupled to mainly Fe-oxide reduction and methanogenesis. Once Fe-oxide reduction starts in the aquifer, As is either desorbed from the surface of the dissolving Fe-oxide or it is released from the mineral structure itself (Nickson et al., 1998, 2000; McArthur et al., 2001; Dowling et al., 2002; Harvey et al., 2002; Swartz et al., 2004). Others have proposed that As is mobilized by displacement from sediment surfaces by HCO₃ generated through the dissolution of carbonate and the reduction of Fe-oxides (Appelo et al., 2002; Anawar et al., 2004), although this mobilization mechanism has been disputed (Radu et al., 2005). Also, Polizzotto et al. (2006) suggested that As is not mobilized within the aquifer but rather in surface soil layers and is subsequently transported down through the sandy aquifer.

One of the problems encountered in the Bangladesh and W. Bengal studies is the extreme variability in the groundwater As content between boreholes only a 100 m apart (van Geen et al., 2003; McArthur et al., 2004). Another problem is the highly complex hydrology of these floodplain aquifers which contain paddy rice fields, dug ponds, irrigation channels and intensified groundwater pumping plain aquifers which contain paddy rice fields, dug ponds, irrigation channels and intensified groundwater pumping systems dominated by organic carbon degradation coupled to mainly Fe-oxide reduction and methanogenesis. Once Fe-oxide reduction starts in the aquifer, As is either desorbed from the surface of the dissolving Fe-oxide or it is released from the mineral structure itself (Nickson et al., 1998, 2000; McArthur et al., 2001; Dowling et al., 2002; Harvey et al., 2002; Swartz et al., 2004). Others have proposed that As is mobilized by displacement from sediment surfaces by HCO₃ generated through the dissolution of carbonate and the reduction of Fe-oxides (Appelo et al., 2002; Anawar et al., 2004), although this mobilization mechanism has been disputed (Radu et al., 2005). Also, Polizzotto et al. (2006) suggested that As is not mobilized within the aquifer but rather in surface soil layers and is subsequently transported down through the sandy aquifer.

### 2. METHODS

#### 2.1. Well construction

Wells with a depth ranging from 5-23 m were constructed using water-jet drilling, and equipped with Ø60 mm PVC-casings, a 0.3 m long screen and 1 m sand trap. The water used for jet drilling was pumped from nearby boreholes or the river. A quartz sand filter pack was installed, and the well was uppermost sealed using bentonite. At the surface a concrete pad (0.5 m x 0.5 m) with a protective steel casing and steel screw cap was constructed. The top end of the PVC-casing was sealed to prevent the entrance of surface water during flooding. Directly after completion the well was pumped to remove the water affected by the drilling operation. Then the well was left at rest for at least three months before sampling.

#### 2.2. Field procedures for sampling and analysis of groundwater

Groundwater was sampled from the boreholes using a downhole pump, a Grundfos MP1 or a Whale pump. Five borehole volumes were flushed before taking the sample. A flow cell equipped with probes for O₂, pH, and electrical conductivity (EC) was mounted directly on the sampling tube. During flushing, the EC and pH were determined after each emptied borehole volume to ensure that stable values were obtained. The measurements were carried out with a WTW Multi197i multi-purpose instrument using a WTW Tetracon 96 EC probe, a WTW SenTix 41 pH electrode and for dissolved O₂ a WTW EO 196-1,5 electrode. Samples for CH₄ were injected directly from the sampling tube through a butyl rubber stopper into a pre-weighed evacuated glass vial, leaving a headspace of one-half to two-thirds of the total volume. After sampling, the vial was immediately frozen, using dry ice, in an upside down position thereby trapping the gas phase above the frozen water. Samples for all other parameters were collected in 50 mL syringes and filtered through 0.2 µm Sartorius Minisart cellulose acetate filters.

Aqueous As(V) and As(III) were separated by filtering the water sample through first a 0.2 µm membrane filter and then a disposable anion exchange cartridge at a flow rate of approximately 6 mL/min using a syringe. The anion exchange cartridge was mounted directly on the filter and the combination was carefully flushed by N₂ before use. The cartridges contained 0.8 g aluminosilicate adsorbent that selectively adsorbs As(V) but not As(III) (Meng and Wang, 1998). Arsenite was determined as the As concentration in the water filtered through a cartridge, and As(V) was calculated as the difference between the total As and As(III) concentrations.

Ferrous iron, phosphate and sulfide concentrations were measured spectro-photometrically in the field using a Hach DR/2010 instrument. Ferrous iron was measured by the Ferrozine method (Stookey, 1970), phosphate using the molybdate blue method and sulfide with the methylene blue method (Cline, 1967) and the detection limits were 1.8, 1.1, and 0.5 µM, respectively.

Alkalinity was determined shortly after sampling by the Gran-titration method (Stumm and Morgan, 1981). Fifty milliliter samples for the cations: Na⁺, Ca²⁺, Mg²⁺, and K⁺ were preserved with 2% of a 7 M HNO₃ solution and refrigerated until analysis in the laboratory. Samples for NH₄⁺, Cl⁻, and SO₄²⁻ were collected in 20-mL polypropylene vials and frozen immediately after sampling.

#### 2.3. Laboratory water analysis procedures

Cations were analyzed by flame atomic absorption spectrophotometry on a Shimadzu AAS 6800 instrument.
Arsenic was determined on the same instrument using a HVG hydride generator and a graphite furnace. Anions were analyzed by ion chromatography using a Shimadzu LC20AD/HIC-20ASuper. NH₄ and SiO₂ were determined spectro-photometrically using respectively the nitroprusside and the ammonium molybdate methods. CH₄ head space concentrations were determined by gas chromatography using a Shimadzu GC-14A with a 1 m packed column (3% SP1500, Carbopack B) and a FID detector. The aqueous methane concentration was calculated using Henry’s law. Detection limits were as follows As 0.013 μM, Mn 0.91 μM, Ca 0.50 μM, NH₄ 5.6 μM, PO₄ 1.1 μM, NO₃ 3.2 μM, SO₄ 2.1 μM, and CH₄ 0.01 mM.

2.4. Sediment sampling and analysis

Sediments were sampled using either a sediment corer or a bailer (1.5 m × Ø110 mm) with a flapper valve. Water from nearby transect boreholes was used to compensate pressure during the drilling. Sediment was collected from the bailer immediately after retrieval by pressing a HDPE-liner (0.5 m × Ø64 mm) up through the sediment contained in the bailer. Any head space in the HDPE-liner was flushed with N₂ and the liners were then sealed with end caps and Al-tape. To further avoid oxygen entrance during storage, the liners were immediately placed in N₂-flushed tubes welded from O₂-diffusion tight Al-laminate. In this state the samples were transported to Denmark where they stayed refrigerated at 10 °C. Sediment subsamples to be used for chemical analysis were freeze dried.

For sequential sediment extractions we used a modified version of the scheme proposed by Wenzel et al. (2001). It was extended with a Na-acetate/acetic acid step to selectively dissolve the carbonate phases (Tessier et al., 1979). Because the As released from the carbonate could adsorb onto the Fe-oxides, the acetate step is followed by a phosphate washing step. The sequential leaching procedure is summarized in Table 1.

Extractions were done in Teflon centrifuge tubes and the tubes were centrifuged at 3000 rpm for 15 min at the end of each step. The supernatant was removed using a syringe and filtered through 0.2 μm cellulose acetate filters. Ca, Fe, and Mn were determined by ICP-OES and As by hydride generation and AAS in a flow injection system (FIHG-AAS), using a Perkin-Elmer 5000 with a deuterium background corrector. Organic carbon was determined as the carbon content of sulphurous acid treated samples using a LECO furnace equipped with an IR225 detector.

2.5. Field site and hydrogeology

A field site was established on the banks of the Red River about 30 km upstream from Hanoi, near the village Dan Phuong. The field site (Fig. 1) is situated on a sand bar between the river and a dyke, which was constructed about 1000 years ago. Agricultural activities here consist of growing crops like corn, beans and sweet potatoes that are not irrigated. There are no paddy rice fields, irrigation channels or pumped wells.

Table 1: Sequential extraction scheme for sediments, modified from Wenzel et al. (2001)

<table>
<thead>
<tr>
<th>Step</th>
<th>Target phase</th>
<th>Extractant</th>
<th>Extraction conditions</th>
<th>SSR [g]/[mL]</th>
<th>Wash step</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Non-specifically bound As</td>
<td>0.05 M (NH₄)₂SO₄</td>
<td>4 h shaking, 20 °C</td>
<td>1:25</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>Specifically bound As</td>
<td>0.05 M (NH₄)H₂PO₄</td>
<td>16 h shaking, 20 °C</td>
<td>1:25</td>
<td>0.05 M (NH₄)H₂PO₄; SSR 1:12.5; 4 h shaking</td>
</tr>
<tr>
<td>3</td>
<td>Carbonate bound As</td>
<td>1 M NaOAc + HOAc, pH 5</td>
<td>6 h shaking, 20 °C</td>
<td>1:25</td>
<td>1 M NaOAc + HOAc, pH 5; SSR 1:25; 4 h shaking</td>
</tr>
<tr>
<td>4</td>
<td>Resorbed As, released from carbonates</td>
<td>0.05 M (NH₄)H₂PO₄</td>
<td>4 h shaking, 20 °C</td>
<td>1:25</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>Amorphous hydrous oxide-bound As</td>
<td>0.2 M NH₄ oxalate buffer, pH 3.25</td>
<td>4 h shaking 20 °C in the dark</td>
<td>1:25</td>
<td>0.2 M NH₄ oxalate, pH 3.25; SSR 1:12.5; 10 min shaking in the dark</td>
</tr>
<tr>
<td>6</td>
<td>Crystalline hydrous oxide-bound As</td>
<td>0.2 M NH₄ oxalate buffer + 0.1 M ascorbic acid, pH 3.25</td>
<td>30 min, water basin at 96 ± 3 °C daylight</td>
<td>1:25</td>
<td>0.2 M NH₄ oxalate, pH 3.25; SSR 1:12.5; 10 min shaking in the dark</td>
</tr>
<tr>
<td>7</td>
<td>As in sulfide minerals</td>
<td>16 N HNO₃ (65%)</td>
<td>Autoclave method 105 min 110 °C</td>
<td>1:25</td>
<td>—</td>
</tr>
</tbody>
</table>

SSR indicates solid-solution ratio.
The local geology shows mainly sandy Holocene deposits down to about 30 m where an up to 4 m thick clay layer marks the transition to Pleistocene sand and gravel deposits. At a depth of 50–60 m, a low permeable Neogene siltstone or sandstone is encountered. The Holocene consists of sandy fluvial deposits formed by point bars and channel fill sediments that are overlain by a confining clay-mud layer, laid down as overbank deposits. The thickness of the confining layer varies from 2 to 10 m and extends to below the channels (Fig. 2). Locally, however, the sand deposits outcrop to the surface, particularly along the banks of the channels. Inspection of the confining layer in such outcrops shows the clay layer to be highly fractured. Comparison with older maps and aerial photographs indicates rapid migration of the sand bars in the Red River and the sand bar at our field site is probably less than a few hundred years old.

Adjacent to the northern channel (Fig. 1) a transect of piezometers was established. One hundred piezometers were installed into the sandy Holocene aquifer, over a total distance of a 100 m (Fig. 2). The boreholes are up to 23 m deep and equipped with a 30 cm long screen. The position of the screens is indicated by the crosses in Fig. 2.

Based on data from a network of piezometers installed in the Holocene sand, the regional ground water flow direction was determined as heading towards 56°, with a predominantly horizontal flow component (Fig. 2) and an average horizontal particle velocity of approximately 17 m/yr. The transect is positioned parallel to the regional groundwater flow direction.

The groundwater table varies from elevation 6 m in the dry season to 8.5 m in the wet season, and along most of the transect, the Holocene aquifer is thus unconfined in the dry and confined in the wet season. In the wet season, from June/July to September/October, water is flowing in the channels from west towards east (Fig. 1), and the water level is directly controlled by the Red River. During the dry period, the water level in the two channels is only partially in contact with the main river through outlets at the eastern end (Fig. 1).

The recharge of the Holocene sand aquifer during the wet season depends on the local thickness of the clay layer. At places where the sand outcrops, the aquifer is filled directly through the sand windows as the river level rises. At other places where the sand does not come to the surface but where the clay cover is thin, recharge may proceed through the fractured clay. The latter is the case at the site of our transect. The annual hydraulic cycle here can be described as follows. During the dry season, the regional flow dominates and the water drains from the uppermost part of the saturated zone. At the onset of the wet season, flow is stalled because the river rises rapidly. At the same time direct recharge to the aquifer takes place through the thin confining clay layer and a local mound with a high hydraulic potential builds up. The unsaturated zone is filled up, and this generates a local vertical component in the groundwater flow direction.

Samples for Tritium/Helium dating of the groundwater were taken from screens placed at different depths in the distance range from 64 to 75 m (Fig. 2). The measurements were performed at Kip Solomon's laboratory at the University of Utah. The results (Fig. 3) suggest the ground waters to be less than 40 years old. The straight line drawn in Fig. 3 is for a downward groundwater velocity of 0.5 m/yr.

In spite of the rather complex recharge conditions it appears that the average flow pattern in the transect can be approximated as behaving like a sandy aquifer with an almost homogeneous infiltration. Seasonally, the sands are filled up with water infiltrating through the clay and the water is then pushed downward. Strong arguments for homogeneous infiltration are, the steady increase in groundwater age over depth (Fig. 3), the horizontal layering in the distribution of stable isotopes (not shown), and the distinct horizontal layering in the groundwater chemistry (discussed in the following). The hydrogeology of the field site will be presented in more detail elsewhere. Here,

![Fig. 2. The transect is orientated approximately SW-NE on the south bank of a side channel to the Red River (Fig. 1). The transect contains 100 piezometers that penetrate the clay cover and are screened at different depth in the underlying sandy Holocene aquifer. The screen length is 30 cm and the screen positions are indicated as crosses in the graph. Arrows indicate the regional flow direction.](image1.png)

![Fig. 3. Groundwater dating using tritium/helium. The samples where taken from boreholes in the distance range 66–75 m (Fig. 2). The water level is at elevation 7.2 m. The line corresponds to a vertical groundwater velocity component of 0.5 m/yr.](image2.png)
we have confined ourselves to a summary to provide the background for the chemical data.

2.6. Geochemical modeling

Speciation calculations and reactive transport modeling were done using the code PHREEQC (Parkhurst and Appelo, 1999). The employed database was for aqueous As based on the compilation of Langmuir et al. (2006).

3. RESULTS

3.1. Water chemistry in the aquifer

Table 2 lists the water composition in the Red River as compared to a typical composition of the water in the Holocene aquifer. The groundwater is a CaHCO$_3$–MgHCO$_3$ type of water, anoxic and enriched in methane. The upper 2 m of the saturated zone contains some O$_2$ but the concentration is significantly lower than the concentration of 0.26 mM (27°C) expected for equilibrium with the atmosphere. At slightly greater depth nitrate and manganese are found at elevated concentration. Nitrate is only found in superficial groundwater at a concentration of up to 0.5 mM and is particularly abundant in the distance range 50–65 m (Fig. 4), where the clay layer is thin. Towards greater depth Fe$^{2+}$ appears in the water and the concentration gradually increases over depth to about 0.3 mM. Up to 0.7 mM of sulfate is found in the uppermost groundwater and its concentration decreases sharply over depth while dissolved sulfide always remains below the detection limit of 0.5 μM. The sulfate distribution indicates that while some originates from the surface, most appears derived from seepage through the river bottom. In the lower part of the aquifer the methane concentration builds up but, in contrast to Fe$^{2+}$, the highest concentration of around 1 mM is found within a horizontal band between elevation 0 and –5 m. The occurrence of sulfate and methane seems mutually exclusive. The uppermost groundwater, down to elevation +3 m is low in ammonia (Fig. 4) but the concentration increases at greater depth. The distribution of ammonia resembles that of methane and at elevation –2 m reaches a maximum of 0.4 mM NH$_4$. Most phosphate is probably released during the reduction of Fe-oxide. The concentration of phosphate is small (<0.01 mM) and while the uppermost oxic groundwater layer has no phosphate, with increasing depth the phosphate concentration gradually increases in a pattern quite similar to that of Fe$^{2+}$.

3.1.1. Redox conditions

Fig. 4 shows the distribution of the main redox sensitive components in the aquifer. The upper 2 m of the saturated zone contains some O$_2$ but the concentration is significantly lower than the concentration of 0.26 mM (27°C) expected for equilibrium with the atmosphere. At slightly greater depth nitrate and manganese are found at elevated concentration. Nitrate is only found in superficial groundwater at a concentration of up to 0.5 mM and is particularly abundant in the distance range 50–65 m (Fig. 4), where the clay layer is thin. Towards greater depth Fe$^{2+}$ appears in the water and the concentration gradually increases over depth to about 0.3 mM. Up to 0.7 mM of sulfate is found in the uppermost groundwater and its concentration decreases sharply over depth while dissolved sulfide always remains below the detection limit of 0.5 μM. The sulfate distribution indicates that while some originates from the surface, most appears derived from seepage through the river bottom. In the lower part of the aquifer the methane concentration builds up but, in contrast to Fe$^{2+}$, the highest concentration of around 1 mM is found within a horizontal band between elevation 0 and –5 m. The occurrence of sulfate and methane seems mutually exclusive. The uppermost groundwater, down to elevation +3 m is low in ammonia (Fig. 4) but the concentration increases at greater depth. The distribution of ammonia resembles that of methane and at elevation –2 m reaches a maximum of 0.4 mM NH$_4$. Most phosphate is probably released during the reduction of Fe-oxide. The concentration of phosphate is small (<0.01 mM) and while the uppermost oxic groundwater layer has no phosphate, with increasing depth the phosphate concentration gradually increases in a pattern quite similar to that of Fe$^{2+}$.

3.1.2. Carbonate dissolution

The compositions of river water and the groundwater differ substantially in their concentrations of Ca, Mg, and HCO$_3^-$ (Table 2), indicating ongoing carbonate dissolution. The uppermost groundwater already contains 3 mM Ca (Fig. 5), much higher than the 0.53 mM Ca in the river water (Table 2). The partial pressure of CO$_2$ in the groundwater ranges from 10$^{-1.1}$ to 10$^{-1.3}$ atm, almost an order of magnitude higher than the $P_{CO_2} = 10^{-1.96}$ atm of the Red River (Table 2). The high $P_{CO_2}$ in the aquifer is due to ongoing decomposition of organic matter and the highest $P_{CO_2}$ values are found in the central zone where methane is also highest. Reactions that specifically produce CO$_2$ are:

\[
CH_2O + O_2 \rightarrow H_2O + CO_2 \quad \text{(1)}
\]

\[
2CH_2O \rightarrow CH_4 + CO_2 \quad \text{(2)}
\]

These reactions are then followed by

\[
CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \quad \text{(3)}
\]

resulting in the high Ca and HCO$_3^-$ concentrations found in the groundwater. The alkalinity increases further with depth probably due to the reduction of Fe-oxides and of SO$_4^-$ by reactions like:

\[
CH_2O + 4FeOOH + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 6H_2O \quad \text{(4)}
\]

and

\[
2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad \text{(5)}
\]

All the groundwater pH values fall within the range from 6.85 to 7.05, which indicate that effective buffering processes are operating. The pH is lowest in the uppermost groundwater and in the central zone around elevation 0 m (Fig. 5), corresponding to the zone where the highest meth-
anel concentration and \( P_{\text{CO}_2} \) values are found (Figs. 4 and 5). Consistently high pH values (>7) are found in the lower part of the aquifer below elevation \(<5\text{ m}\).

3.1.3. Mineral saturation

While the river water is subsaturated for calcite (Table 2) the groundwater (Fig. 6) is close to saturation or slightly supersaturated for calcite. SI values range from 0.0 to 0.45 and the SI_{calcite} distribution patterns seem mostly related to the pH and the inverse of the log \( P_{\text{CO}_2} \) distributions (Fig. 5). It is apparently the coupling to redox processes that makes the groundwater supersaturated for calcite. Particularly, the increase in alkalinity seems related to the Fe\(^{2+}\) distribution and the reduction of Fe-oxides (Eq. (4)) is a plausible cause for the observed slight supersaturation of the groundwater for calcite. The concomitant release of Fe\(^{2+}\) during the reduction of Fe-oxides also causes the saturation index for siderite (FeCO\(_3\)) to increase. The SI_{siderite} gradually increases from \(-0.4\) in the uppermost anoxic groundwater to about 1.6 in the lowermost aquifer corresponding to about forty times supersaturation. Similar high degrees of supersaturation for siderite in aquifers have previously been reported by Postma (1982); Jakobsen and Postma (1999); Swartz et al. (2004) and Jakobsen and Cold (2007). The uppermost water with the highest Mn concentration (Fig. 4) is supersaturated for rhodochrosite (MnCO\(_3\)) (not shown) while further down equilibrium or subsaturation with MnCO\(_3\) is found. Probably Mn is downward removed from the groundwater by carbonate precipitation.

The saturation index for vivianite (Fe\(_3\)(PO\(_4\))\(_2\)·8H\(_2\)O) (Fig. 6) displays a pattern quite similar to that of siderite reaching a saturation index of 1.5. Finally most of the groundwater remains subsaturated for hydroxyapatite (Ca\(_5\)(PO\(_4\))\(_3\)OH) (Fig. 6) in spite of the high Ca concentration and the increase in dissolved phosphate over depth. Only in the bottom few meters of the aquifer reaches the groundwater a weak degree of supersaturation for hydroxy-
apatite. For comparison the Bangladesh groundwaters are more strongly supersaturated for both vivianite and hydroxyapatite because of higher phosphate concentrations (Swartz et al., 2004).

3.1.4. Arsenic

The distribution of As in the groundwater is shown in Fig. 7. The uppermost part of the saturated zone, roughly corresponding to the oxic zone (Fig. 4), contains less than the detection limit of 0.013 μM As. Below that depth the total As concentration gradually increases, reaching values as high as 7.4 μM As or more than 50 times the WHO drinking water limit of 10 μg/L. At the scale of our field site the release of As from the sediment to the groundwater appears homogeneous and shows nothing of the scattered As distribution that has previously been reported from Bangladesh (van Geen et al., 2003). Dissolved As may be present as reduced As(III) or oxidized As(V). Fig. 7 shows that the reduced As(III) form is predominant but a small percentage of As(V) seems always to be present. The distribution of As(III) has a maximum in the middle part of the aquifer and resembles that of ammonia and methane. Particularly in the deepest layers the concentration of As(V), and also its relative proportion of total As seems to increase.

3.2. Arsenic, iron, calcium and carbon speciation in sediments

Sequential extractions were carried out to delineate the speciation of As, Fe and Ca in the sediment, using cores from a borehole at distance 37 m in the transect (Fig. 2).
We used the sequential extraction scheme of Wenzel et al. (2001) extended with steps targeting carbonate dissolution (Table 1) as described in Section 2.4. The results (Fig. 8) show that “Sorbed Ca” resulting from step 1 with (NH₄)₂SO₄ extraction (Table 1) constitutes the largest Ca fraction. It includes Ca adsorbed on exchanger positions and probably some from dissolving carbonate minerals as well. The second step with (NH₄)H₂PO₄ extraction is likely to precipitate any extracted Ca. However, step 3 ("Carb." in Fig. 8) with Na-acetate/acetic acid should dissolve both carbonate minerals and any precipitate resulting from step 2. To be certain of the latter some parallel extractions were done with Na-acetate/acetic acid on untreated sediment. The results were within 5% of those obtained with the sequential procedure. The “Carb” (step 3) fraction particularly extracts a pool of Ca between elevation 0 and −5 m. Finally, “Total” reflects the additional amount of Ca extracted by HNO₃ (Table 1) which will dissolve any remaining carbonate and extract some Ca from silicate minerals as well. For Fe (Fig. 8) the amorphous hydrous oxide (step 5) and the crystalline Fe-oxide (step 6) fractions (Table 1) extract about equal amounts of Fe although the former tends to increase somewhat over depth. Some caution is warranted in the interpretation of extracted Fe in terms of amorphous and crystalline Fe-oxides as even small amounts of Fe²⁺ in combination with oxalate will catalyze the dissolution of more crystalline Fe-oxides like goethite and hematite (Suter et al., 1988). Because Fe²⁺ is present in the groundwater, and therefore probably also in our sediments,
step 5 is likely to extract much more Fe than what is bound as amorphous Fe-oxides. Finally, the total Fe (step 7) fraction will extract Fe from pyrite and silicates. The peaks in the Fe distribution at elevations +6 and +11 m correspond to the presence of clay layers.

The distribution of As (Fig. 8) shows that “Sorbed” As (steps 1 + 2 in Table 1) only constitutes a small part of the extracted As. The fraction of As specifically derived from carbonates (“Carb.” in Fig. 8) is negligible and the zone between elevation 0 and −5 m where the Ca distribution indicates that most carbonate dissolution takes place is not at all reflected in the As distribution. Accordingly there is no evidence to support the association of As with CaCO₃ phases in the sediment. By far most of the As is extracted in the two steps (5 and 6) targeting Fe-oxides. As for iron, the As distribution shows peaks where there are clay layers in the sediment. There is also a trend showing the highest As values above the water table, and then somewhat decreasing with depth below the water table. Some additional As is extracted by HNO₃ (“Total” in Fig. 5) which could be derived from pyrite and silicate minerals. However, the general conclusion is that most As must be associated with the Fe-oxide fraction in the sediment.

Various schemes for the extraction of As from sediments have been published, and these have recently been reviewed by Hudson-Edwards et al. (2004). Basically extractions schemes are empirically defined and likely to give somewhat different results. Thus Swartz et al. (2004) used the extraction scheme of Keon et al. (2001) to investigate the As speciation of Bangladesh aquifer sediments. However, regardless of any method differences, there is no doubt that the sediments at Dan Phuong are richer in As than those in Bangladesh. Swartz et al. (2004) reported total As concentrations generally to be less than 3 μg/g. Dowling et al. (2002) used an oxalate extraction on Bangladesh aquifer sediment and found As concentrations at the same level. In Dan Phuong, we find total concentrations between 7 and 12 μg/g, except for the uppermost clay layer where 20 μg/g As was found, and our extraction scheme does not even include the harsh extraction steps where Swartz et al. (2004) found a significant part of the As. Both in Swartz et al. (2004) and our study the desorbable amount of As is on the order of 1 μg/g and the real difference is in the amount of As associated with the Fe-oxide fractions. The total amount of Fe in the sediment is in both studies found to be around 20 mg/g, but Swartz et al. (2004) found that only 5–10% was associated with Fe-oxide phases, while we find that more than 50% of the 20 mg/g represents Fe-oxide phases. Since the titanium(III)chloride–sodium citrate–tetrasodium EDTA–bicarbonate method used by Swartz et al. (2004) to extract “crystalline” Fe-oxide is more harsh then our 0.2 M oxalate–0.1 M ascorbic acid treatment (Table 1), the Dan Phuong sediments must be more rich in Fe-oxides, with associated As, than the Bangladesh aquifer sediment studied by Swartz et al. (2004).

Finally, the organic carbon content in six sediment samples from the same cores was determined. The organic carbon content ranged from 0.04% to 0.74% C with an average of 0.27% C.

**4. DISCUSSION**

### 4.1. Degradation of organic matter and arsenic mobilization

The groundwater chemistry at Dan Phuong indicates the degradation of organic matter to be an important process in the aquifer. The overall picture is a classical redox sequence with the degradation of organic matter proceeding sequentially through different electron acceptors (Appelo and Postma, 2005). After the reduction of dissolved oxygen, nitrate and Mn-oxides become reduced (Fig. 4). This is again followed by the reduction of Fe-oxides and sulfate. The final process in the redox sequence is fermentation of organic material, leading to the release of methane to the groundwater.

The distribution of As (Fig. 7) seems closely related to the changing redox conditions in the aquifer. The uppermost, least reduced layers are free of As, while the As concentration increases as the waters become more reducing. The distribution of As(III) seems strongly related to the distributions of methane and ammonia (Fig. 4). All three components show a maximum between elevation 0 and −5 m suggesting a flow path richer in reactive organic matter. Further down the concentration of As(V) increases while the methane concentration decreases. An intuitive interpretation would be that the conditions near the bottom of the transect become less reducing. To further explore this we used PHREEQC to calculate the $pe$ for the As(III)/As(V) and CH₄/CO₂ redox couples. The $pe$ values calculated from both half-reactions are shown in Fig. 9 and for both redox couples the $pe$ appears to decrease gradually without any indication of an increase in $pe$ near the bottom of the transect. In terms of dominant species the reactions for the As(III)/As(V) and CH₄/CO₂ redox couples can be written as:

![Fig. 9. The redox state, given as $pe$, calculated for the As(V)/As(III) and CH₄/CO₂ redox half reactions from the field data. The calculations were done using PHREEQC.](image-url)
\[ \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{AsO}_4^- + 3\text{H}^+ + 2e^- \quad \text{(6)} \]
\[ \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightarrow \text{HA}_3\text{O}_4^- + 4\text{H}^+ + 2e^- \quad \text{(6a)} \]

and
\[ \text{CH}_4 + 3\text{H}_2\text{O} \rightarrow \text{HCO}_3^- + 9\text{H}^+ + 8e^- \quad \text{(7)} \]

Eqs. (6) and (7) show how at a given \( \text{pH} \) the distribution between oxidized and reduced species also is a function of the \( \text{pH} \). An increase in \( \text{pH} \) at constant \( \text{pH} \) will therefore favor a decrease in the As(III)/As(V) and CH\(_4\)/CO\(_2\) ratios. The presence of As(V) in the groundwater is consistent with the concept that As is released as As(V) from the iron oxides and subsequently is reduced to As(III) (Islam et al., 2004). Comparison of the calculated \( \text{pH} \) for the As(III)/As(V) and CH\(_4\)/CO\(_2\) couples shows that the latter are about 3 \( \text{pH} \) units lower than the former. This indicates disequilibrium between the different redox couples as previously observed by Jakobsen and Postma (1999).

Nitrogen compounds are contained in natural organic matter and upon decomposition it is released as ammonia to the groundwater. The ammonia concentration is therefore a good indicator for the intensity of organic matter degradation as illustrated by the correlation between ammonia and methane shown in Fig. 10. When Fe\(^{2+}\) is released as the result of the reduction of Fe-oxides by the same organic matter (Eq. (4)) then the increase in Fe\(^{2+}\) over depth should also be correlated with the NH\(_4\) concentration. However, comparison of the reaction stoichiometry in Eqs. (2) and (4) shows that the increase in concentration per mmol of NH\(_4\) should be 8 times higher for Fe\(^{2+}\) as compared to CH\(_4\). Indeed Fig. 10 shows a very steep initial increase in the Fe\(^{2+}\) concentration with increasing NH\(_4\). However, as the Fe\(^{2+}\) concentration exceeds 0.2 mM it appears as if a barrier against further increases in Fe\(^{2+}\) is reached and this results in a lot of data scatter. In contrast the correlation between the groundwater As(III) concentration and the ammonia concentration is excellent, as previously observed by Harvey et al. (2002) in Bangladesh. This strongly indicates that the As release to the groundwater is directly coupled to the degradation of organic matter. Plotting total As instead of As(III) in Fig. 10 would show almost the same general pattern.

![Fig. 10. Correlation between ammonia, as indicator for organic matter degradation and other parameters in the groundwater of the Dan Phuong transect (Fig. 2).](image-url)
Dowling et al. (2002) showed that the As content of the organic matter is very low and therefore an unlikely source of groundwater As. In addition, in our sediment (Fig. 8) As appears to be associated with Fe-oxides. The most reasonable interpretation is therefore that the reductive dissolution of As-containing Fe-oxides coupled to the oxidation of organic matter is the cause of the release of As to the groundwater in agreement with previous studies (Nickson et al., 1998, 2000; McArthur et al., 2001; Dowling et al., 2002; Harvey et al., 2002; Swartz et al., 2004).

Since both the Fe$^{2+}$ and the As concentrations are correlated with the NH$_4$ concentration, the two must also be correlated internally as well. The resulting correlation between Fe$^{2+}$ and As(III) (Fig. 10) has often been used as an argument for the release of As by reductive dissolution of Fe-oxides (McArthur et al., 2001, 2004; Dowling et al., 2002; Smedley and Kinniburgh, 2002; Horneman et al., 2004; van Geen et al., 2006). For the Dan Phuong aquifer the Fe$^{2+}$/As(III) correlation is good at low values but shows a good deal of scatter at higher values. As argued above, the NH$_4$/Fe$^{2+}$ plot in Fig. 10 indicates that a maximum for the Fe$^{2+}$ concentration is reached, suggesting that part of the produced Fe$^{2+}$ is precipitated as a Fe(II) phase. Sengupta et al. (2004) identified extensive precipitates of siderite in Bangladesh sediments and since the groundwater at Dan Phuong reaches high supersaturation for siderite (Fig. 6) this mineral could be a Fe(II) sink at Dan Phuong as well. The Si$_{siderite}$ is largely controlled by the Fe$^{2+}$ concentration (Fig. 11) because the alkalinity and the pH do not vary much (Fig. 5).

Siderite precipitation is very slow at low temperatures but Postma (1982) presented field evidence for siderite precipitation once the Si$_{siderite}$ exceeded 1. At Dan Phuong the Fe$^{2+}$/As(III) ratio is found to decrease sharply once the Si$_{siderite}$ exceeds 1 (Fig. 11) which also indicates that siderite precipitation is taking place. Sengupta et al. (2004) suggested the precipitation of siderite to be a mechanism for As removal from the groundwater by coprecipitation and adsorption. Our data indicates that whatever the Fe(II) precipitate is, it removes proportionally more Fe$^{2+}$ than As(III) (Fig. 11).

### 4.2. Arsenic desorption and mobilization

Desorption of As from the sediment is another mechanism that could release As to the groundwater. Polizzotto et al. (2006) found about 15% of the solid phase As to be easily desorbed and they proposed an As mobilization process where As is released to water in surface soil/sediments and is subsequently transported down into the aquifer. Appelo et al. (2002) and Anawar et al. (2004) suggest the displacement of As by HCO$_3$ from the sediment surface exchange complex to be the As mobilization mechanism. In this scenario the reduction of Fe-oxides (Eq. (4)) and the dissolution of carbonate (Eq. (3)) produce the bicarbonate that triggers the desorption of As. Appelo et al. (2002) used a modified version of the Dzombak and Morel (1990) surface complexation model to illustrate the desorption of As. However, Swartz et al. (2004) showed for a Bangladesh aquifer that when silica is incorporated in the surface complexation model, the high silica content of the groundwater causes most of the surface complex to become covered by predominantly silica and therefore the ability of bicarbonate to displace As becomes limited. In a recent experimental study, Radu et al. (2005) found that bicarbonate had little effect on As(V) sorption.

The data of the Dan Phuong aquifer is in conflict with the model proposed by Polizzotto et al. (2006) because at our site the As concentration builds up gradually over depth in the aquifer (Fig. 7) as conditions become more reducing and no leaching of As out of the soil is observed. Fig. 12 shows the relative composition of the surface complex for a representative sample in the middle of the Dan Phuong aquifer (sample H51, Table 2) calculated using the Dzombak and Morel (1990) surface complexation model extended with carbonate (Appelo et al., 2002) and silica species (Swedlund and Webster, 1999). The weak adsorption sites are dominated by carbonate species (48%) and silica species (31%) while strong sites do not adsorb anions. Arsenite covers about 3% of the surface sites and adsorbed...
As(V) is negligible. For comparison the surface complex composition of Bangladesh aquifer sediment, calculated by Swartz et al. (2004), was dominated by about 56% silicate species, 28% carbonate species and 6% As(III). The difference is mainly due to the much higher silica concentrations in the Bangladesh groundwater.

In the Dan Phuong aquifer most bicarbonate seems to be derived from carbonate dissolution occurring already in the soil or in the unsaturated zone (compare with the river water composition in Table 2). Accordingly, the uppermost groundwater already has a high bicarbonate concentration (Fig. 5) but contains no As (Fig. 7). If the mechanism of As mobilization was simple displacement by bicarbonate, this process should already proceed in the uppermost part of the aquifer. Finally, the theories of desorption or reduction of Fe-oxides as mechanisms for As mobilization need not to be mutually exclusive. Pedersen et al. (2006) showed experimentally how As released from the Fe-oxide structure during dissolution did adsorb to the surface of the remaining Fe-oxides.

4.3. Reactive transport modeling

Fig. 3 shows how the age of the groundwater uniformly increases over depth. In addition the water chemistry shows (Figs. 4–7) a distinct horizontal layering indicating that as the groundwater residence time increases, the geochemical reactions change the water composition. For a sandy aquifer with homogeneous infiltration, the water at each depth level will have the same age (Appelo and Postma, 2005) and this allows us to analyze the development in water chemistry over time by constructing a one-dimensional reactive transport model for the vertical component of the groundwater movement only. It corresponds to projecting the water chemistries along the different flow paths into a single vertical profile. Reactive transport models based on this principle have previously been published for nitrate reduction (Postma et al., 1991), the degradation of organic matter (Jakobsen and Postma, 1999) and for groundwater acidification (Kjøller et al., 2004).

Fig. 12. The relative composition of the surface complex calculated from the composition of a representative sample (sample HS1, Table 2) using PHREEQC with the Dzombak and Morel (1990) surface complexation model extended with surface species for carbonate (Appelo et al., 2002) and silica (Swedlund and Webster, 1999).

4.3.1. Redox zonation

The model for the redox zonation is based on the partial equilibrium approach proposed by Postma and Jakobsen (1996). In this approach the degradation of organic carbon is the only rate controlling parameter, while internal equilibrium is assumed among all the electron accepting processes and methanogenesis. Organic carbon is a sediment property in the model and the degradation rate in a given cell is a constant during the model run. The rate of organic matter degradation is determined by fitting the model to the field data. In the uppermost meter of the aquifer the modeled rate of organic matter degradation is 0.075 mmol C/L/yr while for greater depth a constant rate of 0.15 mmol C/L/yr was found. These rates are expressed per liter of groundwater in contact with the sediment. Also the solubility of the iron oxides is determined by trial and error. In the upper 3 m the solubility of the iron oxide, expressed as $K = \frac{[Fe^{3+}] [OH^-]^{\frac{3}{2}}}{[Fe(OH)_3]}$, is $10^{-40}$ while at greater depth it is kept constant at $10^{-24}$. Equilibrium with calcite with an $SI = 0.2$ was assumed in compliance with the field data (Fig. 6). FeS was allowed to precipitate when its solubility product was exceeded. Siderite precipitation is allowed once an SI of 1.4 is exceeded. The initial solution used in the model is Red River water (Table 2) equilibrated with a CO$_2$ partial pressure of $10^{-13}$ atm and calcite with SI = 0.2.

The model results are compared with the field data in Fig. 13 and generally there is good agreement. The model correctly describes both the relative appearance and disappearance of the different redox components as well as their concentration levels. With increasing depth, first O$_2$ disappears, thereafter NO$_3$ becomes reduced, followed by an increase in Fe$^{2+}$ due to the reduction of Fe-oxide, the decrease in SO$_4$ due to sulfate reduction and finally methanogenesis occurs concomitantly with further reduction of Fe-oxides. All H$_2$S produced by sulfate reduction is precipitated as FeS. As outlined in Section 3.1.2., these redox reactions are closely interrelated with carbonate reactions through CO$_3$ and HCO$_3$ production and carbonate mineral dissolution and precipitation. The carbonate components (pH, alkalinity, P$_{CO_2}$ and Ca) are generally well described by the model. However in the lower part the model slightly underestimates the alkalinity. Possibly this is due to neglecting some silicate weathering, for example of biotite, since both Mg and Si (not shown) increase slightly over depth.
The two critical parameters controlling the position and extension of the different redox zones are the rate of organic matter degradation and the stability of the Fe-oxide being reduced. Both are found by fitting the model to the field data and even small variations in these two parameters cause significant displacement of the redox zones and a poor match with the pH, alkalinity and $P_{CO_2}$. The rate of organic matter degradation is 0.15 mmol C/L/yr, except in the uppermost cell where it is half of this value, and is for a Holocene aquifer not very high (Appelo and Postma, 2005). Jakobsen and Postma (1999) and Hansen et al. (2001) found for a Holocene aquifer in Denmark a rate that was up to an order of magnitude higher and in addition highly variable over depth. On that background it is surprising that the Dan Phuong aquifer can be modeled with a constant rate of organic carbon degradation in all but the uppermost meter of the aquifer. The lower organic matter degradation rate required to fit the field data in the uppermost meter of the aquifer probably reflects episodic exposure of the sediment organic matter to atmospheric oxygen during fluctuations in the water table. The model results are strongly dependent on the stability used for the Fe-oxides being reduced. In the upper 3 m we could match the field data by using a stability of iron oxide of $K = 10^{-40}$, which corresponds to lepidocrocite or a poorly crystalline goethite. In the remaining 17 m long deeper part, we used a constant value of $K = 10^{-42}$, corresponding to a well crystalline goethite or a hematite. The slightly higher solubility...
of the Fe-oxides in the upper 3 m could be due to reoxidation of groundwater Fe\(^{2+}\) followed by precipitation during annual fluctuation in the water table. The most stable Fe-oxides must be expected to have a low reactivity (Larsen and Postma, 2001). However according to our model the rate of organic carbon degradation is even slower and is therefore overall rate limiting. The high stability of the Fe-oxides in the sediment also explains the observed deviations from the standard redox sequence. Thus both the field data and the model indicate that sulfate reduction is complete before iron reduction. As shown by Postma and Jakobsen (1996) sulfate reduction becomes energetically more favorable compared to iron reduction in the presence of stable Fe-oxides as opposed to the situation when the more unstable ferrihydrite is being reduced. Likewise the field data shows iron reduction to proceed together with methanogenesis and again in our model this is only possible when the stability of the Fe-oxides present is high. The cumulative amount of Fe-oxide that dissolves in any model cell is not more than 0.03 mg Fe per gram sediment. This value can be compared with the values (Fig. 8) for Fe-oxide bound iron in the sediment, giving values around 10 mg Fe/g sediment indicating that the source of Fe-oxide for reduction will not become depleted for many pore volumes.

Below elevation 2 m the \( S_{\text{sat}} \) exceeds 1.4 and our model starts to precipitate siderite. This high barrier for siderite precipitation complies with the field data and reflects the strong inhibition of siderite precipitation earlier observed in the field (Postma, 1982; Jakobsen and Postma, 1999; Jakobsen and Cold, 2007). The highest amount of siderite accumulated in any model cell over the modeled 40 year period is 0.035 mg Fe/g sediment and again this amount is small as compared to measured iron content in the sediment (Fig. 8). Most dissolution of calcite apparently occurs during the initial equilibration of the Red River water, where the Ca concentration increases from the initial 0.5 to 3 mM. Further downward only small amounts of calcite are dissolved or precipitated. Over the modeled 40 year period the gain or loss of calcite from the sediment in any cell only varied between +0.03 to −0.02 mg CaCO\(_3\)/g sediment.

### 4.3.2. Arsenic

In the model, As(V) was incorporated as a minor constituent of the Fe-oxide being reduced. Optimization showed that an As/Fe molar ratio of 0.0025 in the dissolving oxide gave results that are in agreement with the field data. When the model reduces Fe-oxide by organic carbon oxidation, As(V) is released. Since As(V) is unstable under the prevailing reducing conditions it will be reduced to As(III). The model predicted gradient of As increase over depth depends, in this set-up, on the As content in the Fe-oxide and the rate of Fe-oxide reduction. The aqueous As may adsorb onto the surface of the remaining Fe-oxides. To model the sorption of As on Fe-oxides we used the Dzombak and Morel (1990) surface complexation model that is available in PHREEQC. The standard Dzombak and Morel (1990) model is for ferrihydrite but as discussed in the previous section, modeling the redox zonation suggest that the Fe-oxides in the Dan Phuong sediments are of a much more stable type, rather like goethite or hematite which have a much lower specific surface area. It is therefore reasonable that the default value of 0.2 mol weak sites per mole of Fe valid for ferrihydrite is reduced significantly. Using a sediment Fe-oxide concentration of 10 mg Fe/g sediment, which corresponds to 1 mol Fe per liter of contacting groundwater, the fitted number in our model becomes 0.1 nmol weak sites per mol of Fe-oxide. Also Swartz et al. (2004) had problems in fitting the Dzombak and Morel (1990) model to their field data. Instead of reducing the number of sites per mol of Fe, they reduced the amount of Fe entered in the model and found that when only 2.5% of the measured oxalate extractable Fe content was used, while using the standard number of weak sites per mol Fe, then they could reproduce the As speciation between water and sediment. The Dzombak and Morel (1990) model has a fixed ratio between weak sites and strong sites. However, the fitted number of weak sites corresponds to a strong sites concentration that is too low to influence on the bulk water chemistry.

Fig. 13 compares the model results with the field data, after one pore volume has been transported corresponding to 40 years. Modeled As(III) is seen to enter the groundwater at the same depth level as Fe\(^{2+}\), it increases over depth until a maximum is reached at elevation −5 m and then decreases towards greater depth. Generally, modeled As(III) is in good agreement with the field data. For As(V) the model predicts concentrations that are close to zero while in the field concentrations of up to 2 \( \mu \text{M} \) As(V) were measured. The partial equilibrium model is able to describe the redox speciation for all main components, indicating that internal equilibrium between the different electron accepting processes is closely approached. The model predicted \( \text{pe} \) is also in good agreement with the \( \text{pe} \) calculated for each water sample from the \( \text{CO}_2/\text{CH}_4 \) concentrations (Fig. 13). However, the \( \text{pe} \) calculated from the measured As(V) and As(III) values is about three units higher than the model predicted \( \text{pe} \) values. Similar to the other terminal electron accepting processes the reduction of As(V) is probably microbial catalyzed and As(V) respirers are present in our sediments (Heimann et al., 2007). But apparently, the reduction of As(V) to As(III) does not attain equilibrium with the other terminal electron accepting processes. The non-equilibrium behavior of As(V)/As(III) was already noted by Cullen and Reimer (1989) and As(V) has also been found in permanently anoxic lake waters (Seyler and Martin, 1989; Aurillo et al., 1994; Oremland et al., 2000).

In the model the As/Fe ratio of the dissolving oxide is 0.0025 while in oxalate extractions a As/Fe ratio of about 0.0008 was measured. Although these numbers only differ by a factor of three, it still indicates that As is not homogeneously distributed in the sediment pool of Fe-oxide. The maximum total amount of As removed from any model cell due to Fe-oxide dissolution corresponds to 0.12 \( \mu \text{g} \) As/g sediment which remains small compared to the analyzed concentration of As associated with Fe-oxide, of around 5 \( \mu \text{g} \) As/g sediment (Fig. 8). The concentration of the aqueous As(III) in the model is about equal to the sorbed concentration. The fraction of the surface sites covered by As is at maximum 0.05, result-
ing in an adsorption isotherm for As that is close to linear. The maximum modeled sorbed concentration is around 0.06 µg As/g sediment and falls within the range of 0.02–0.21 µg As/g sediment extracted as “Non-specifically bound As” in step 1 of the extraction scheme (Table 1).

The redox model is at pseudo steady state, the rate of organic matter is constant in each cell and the initial amount of As-containing Fe-oxide of 1 mol/L contacting groundwater is so large that it will not change significantly during the model run. The fact that this very simple model with a constant organic matter degradation rate in 19 out of 20 cells and a constant Fe-oxide stability in 17 out of 20 cells describes the field data so well suggests that stationary redox conditions are also prevalent in the field. On the other hand the modeled dissolved As profile is transient because after displacement of only one pore volume the effects of As sorption are still visible. The model results (Fig. 13) show a peak in dissolved As(III). On the downward side of the peak As(III) is sorbed and becomes retarded. However, on the upward side of the peak there is a steady supply of As by further reduction of As containing Fe-oxide. When the model is run forward it takes the replacement of about two pore volumes before a steady situation arises between the solution and the surface complex. In that case the continued release over depth of As by Fe-oxide reduction will cause a steady increase in the As concentration. Once the As gradient becomes stationary, sorption will have no further retarding effect on As transport through the aquifer. Typically many As contaminated aquifers are situated in young flood plain systems, with low gradients and are therefore poorly flushed. Such young systems are particularly liable to display transient As distributions in the groundwater due to sorption.

4.4. Comparison with Bangladesh aquifers

The Dan Phuong aquifer is situated on the floodplain of the Red River which flows from the Himalayas and into the Gulf of Tonkin. The sediments have a similar origin and environment of deposition as the Holocene floodplain sediments along the Ganges and Brahmaputra delta that contain the aquifers in Bangladesh and W. Bengal and a comparison seems therefore warranted. Because our field site at Dan Phuong is located between the river and the dyke, the sediments are very young, probably less than a few hundred years old. The sediments in Bangladesh have been deposited during the entire Holocene and Goodbred and Kuehl (2000) report radiocarbon ages between 2000 and 10,000 year BP. Therefore processes leading to the release of As to the groundwater have been going on for a much longer period of time in Bangladesh and perhaps the Dan Phuong aquifer can be viewed as a kind of initial state for the Bangladesh aquifers.

The model for Dan Phuong indicates the rate of sedimentary organic carbon degradation to be overall rate controlling for the As release, as it controls the rate of Fe-oxide reduction and thereby the rate of As release to the groundwater. A similar conclusion was reached for Bangladesh aquifers by McArthur et al. (2001). Harvey et al. (2002) injected highly reactive dissolved organics into a Bangladesh aquifer which resulted in an increase of the groundwater As concentration. This result confirms the reactivity of organic carbon to be the rate controlling parameter for the As release. Because the reactivity of the sedimentary organic matter will decrease over time as the most reactive part is consumed (Appelo and Postma, 2005) the rates of organic matter degradation in the Bangladesh aquifers must be expected to be lower as compared to Dan Phuong. Unfortunately, the change in the rate of organic carbon degradation over time is unknown and this essentially obstructs a meaningful projection of the long time behavior of the Dan Phuong aquifer. However, a simplified first assessment in the comparison of the Dan Phuong and Bangladesh aquifers can still be done using the present day rates, which will represent maximum rate estimates, and the pool sizes of organic carbon, Fe-oxide and As.

The average content of organic carbon is 0.27% C, corresponding to 1.4 mol C per liter of groundwater. Dividing this number by the modeled organic matter degradation rate of 0.15 mmol C/L/yr. yields 9300 years, which is quite close to the start of the Holocene.

The model predicts that at maximum 0.03 mg Fe per gram sediment is removed during one pore volume of 40 years. Extrapolating to 10,000 years, the approximate age of the Bangladesh aquifers, 7.5 mg Fe/g sediment will be reduced corresponding to about 75% of the total pool of about 10 mg Fe/g initially present as Fe-oxide in the sediment (Fig. 8). For As, the model predicts that at maximum 0.12 µg As/g sediment is removed from the solid phase during one pore volume of 40 years. Extrapolating again to 10,000 years this implies a As release to the groundwater of 30 µg/g sediment. However, comparison with Fig. 8 shows that this is about three times the analyzed amount which is of course unreasonable. Clearly the projection forward in time, based on constant rates, is rather crude. What still can be learned, however, is that on a 10,000 years time scale it can be expected that a rather large part of the carbon, arsenic and Fe-oxide can be removed from the sediment. This prediction is consistent with the comparison of sediment As and Fe-oxide contents given in Section 3.2.

Somewhat surprisingly our model indicates that the Fe-oxide being reduced is not a poorly crystalline iron oxyhydroxide, such as ferrihydrite but rather more stable and better crystalline Fe-oxides like goethite or hematite. Except for the results from chemical extractions, which are not really mineral specific, there is not much direct evidence of the binding of As to Fe-oxides in the aquifer sediments of W. Bengal and Bangladesh. Gault et al. (2003) used EXAFS to investigate W. Bengal sediment and found the presence of As(V), either sorbed to the surface or incorporated in Fe-oxides. Akai et al. (2004) report from Bangladesh aquifer sediments the occurrence of Fe-oxides with variable As contents by using EPMA. On the other hand Polizotto et al. (2006), studying Bangladesh aquifer sediment using µ-XRF and µ-XANES, did not succeed in identifying As bound to Fe-oxides. The presence of more stable Fe-oxides in the aquifer sediment could also be the result of a catalytic transformation from precursors like ferrihydrite in the presence of Fe²⁺ when the system goes anoxic (Pedersen et al., 2005; Herbel and Fendorf, 2006). Pedersen et al. (2006)
found that while As(V) coprecipitated with ferrihydrite remained at the mineral surface, and was easily desorbed, for the better crystalline goethite a large part of the As was incorporated in the crystal structure and not easily desorbed. This again may explain why the As is not desorbed from the sediment as the HCO₃⁻ concentration increases in the uppermost part of our aquifer, the mechanism suggested by Appelo et al. (2002), but is first released when the bulk Fe-oxide becomes reduced. Under transient conditions sorption is probably still important to understand the As distribution in these young aquifers.

5. CONCLUSIONS

The groundwater geochemistry at Dan Phuong, in a young Holocene aquifer on the banks of the Red River, displays a rapid mobilization of As. Apparently the As is released from the floodplain sediment in relation to organic matter degradation. The measured groundwater As concentration did exceed 500 µg/L or 50 times the WHO limit! The uniform increase in As in the groundwater over depth suggests that the problem with high As may be widespread in Holocene aquifers of the Red River flood plain and should be taken very seriously.

The main mechanism for As mobilization seems to be the reduction of Fe-oxide by sedimentary organic matter. Modeling indicates that the Fe-oxides being reduced are not poorly crystalline oxyhydroxides but rather are more crystalline phases with a stability in the range goethite or hematite. Our model also indicates that the As initially is not present in an easily desorbed form on the surface of the Fe-oxides but rather firmly bound within the Fe-oxide structure and only upon bulk reductive dissolution is the As released to the groundwater. Part of the As(III), however, is readorsed to the surface of the remaining Fe-oxides.

The overall rate controlling factor for the reduction of the Fe-oxides, and thereby for the release of As, is the activity of the organic matter present in the sediment. Our model indicates that the rate of organic carbon degradation is low and surprisingly constant, near 0.15 mmol C/L/yr, and given the pool size of the As bearing Fe-oxide the release of As to the groundwater may continue for thousands of years.

The groundwater As distribution is, apart from the release of As from Fe-oxide during reductive dissolution, also dependent on sorption to the Fe-oxide surface. Modeling indicates the sorption capacity of the sediment to be low, but sorption will still affect the As distribution for at least the first two pore volumes that flush the aquifer. Thus, while the reductive release of As to the groundwater is more or less stationary, due to sorption, the As distribution becomes transient changing significantly over time and place.

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