Controlling geological and hydrogeological processes in an arsenic contaminated aquifer on the Red River flood plain, Vietnam

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A B S T R A C T

Geological and hydrogeological processes controlling recharge and the mobilization of As were investigated in a shallow Holocene aquifer on the Red River flood plain near Hanoi, Vietnam. The geology was investigated using surface resistivity methods, geophysical borehole logging, drilling of boreholes and installation of more than 200 piezometers. Recharge processes and surface–groundwater interaction were studied using (i) time-series of hydraulic head distribution in surface water and aquifers, (ii) the stable isotope composition of waters and (iii) numerical groundwater modeling. The Red River and two of its distributaries run through the field site and control the groundwater flow pattern. For most of the year, there is a regional groundwater flow towards the Red River. During the monsoon the Red River water stage rises up to 6 m and stalls the regional groundwater flow. The two distributaries recharge the aquifer from perched water tables in the dry season, whilst in the flooding period surface water enters the aquifer through highly permeable bank sediments. The result is a dynamic groundwater flow pattern with rapid fluctuations in the groundwater table. A transient numerical model of the groundwater flow yields an average recharge rate of 60–100 mm/a through the confining clay, and a total recharge of approximately 200 mm/a was estimated from 3H/3He dating of the shallow groundwater. Thus in the model area, recharge of surface water from the river distributaries and recharge through a confining clay is of the same magnitude, being on average around 100 mm/a. The thickness of the confining clay varies between 2 and 10 m, and affects the recharge rate and the transport of electron acceptors (O2, NO3 and SO4 2-) into the aquifer. Where the clay layer is thin, an up to 2 m thick oxic zone develops in the shallow aquifer. In the oxic zone the As concentration is less than 1 μg/L but increases in the reduced zone below to 550 μg/L. In the Holocene aquifer, As is mobilized at a rate of around 14 μg/L/a. An As mass balance for the field site shows that around 1100 kg of As is annually leached from the Holocene sand and discharged into the Red River, corresponding to 0.01% of the total pool of As now present in the Holocene sand.

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1. Introduction

Groundwater enrichment by geogenic As is a widespread problem in the flood plain aquifers of Southeast Asia. Ultimately the source of As is the transport of As-containing sediments from the Himalayas down to the flood plains (Stanger, 2005; Charlet and Polya, 2006). On a regional scale, the distribution of high-As waters in West Bengal and Bangladesh shows great variation due to differences in sediment distribution, diagenesis and variations in abstraction depths (Smedley and Kinniburgh, 2002). On a smaller scale, the patchy distribution of As in groundwaters of Bangladesh is influenced by the complex hydrology of paddy rice fields, irrigation channels and boreholes and waste water ponds. These produce a mosaic of recharge and discharge areas resulting in complex groundwater flow paths and variable As distribution (Harvey et al., 2006). The more detailed coupling of As enrichment to groundwater hydraulics has only recently been addressed (e.g. Klump et al., 2006; Stute et al., 2007). Klump et al. (2006) made a rigorous analysis of how irrigation pumping is affecting the flow system in the upper 30 m of the aquifer. Stute et al. (2007) studied the hydrological control on the groundwater As concentration in Bangladesh and reported an increase in the As concentration with increasing groundwater age for the upper 20 m of the aquifer. Although the mechanism of As release from the sediments is still uncertain, the relationship between the As concentration and groundwater age suggests the kinetics of As release from the sediments and the groundwater residence time to be important factors (Stute et al., 2007).

High groundwater As concentrations have also been reported from aquifers of the Red River flood plain, Vietnam (Berg et al., 2001, 2008). The objective in this study is to clarify the hydrogeological and geochemical processes controlling the mobilization of As in a Red River Holocene aquifer. The field site is near the village Dan Phuong, 30 km NW of Hanoi. The geochemical results of the study have been published by Postma et al. (2007). The field site (Fig. 1) is located between the dyke and the Red River and is intersected by two minor distributaries to the Red River. Between the dyke and the river there is no groundwater abstraction and therefore the natural interaction between the surface waters and the shallow aquifer can be studied. The study addresses the hydrogeology and As mobilization in a Holocene aquifer to a depth of 22 m below the surface.

Fig. 1. Location of the Dan Phuong field site, 30 km NW of Hanoi on the Red River flood plain (UTM coordinates: 565695; 2338909). The location of boreholes is indicated by dots except for those contained in the H- and the K-transects which each contain up to 100 piezometers. The orientation of the geological cross-section in Fig. 4 is shown as the line A–B, and the model domain for the numerical groundwater model is also indicated.
Here the results of the geological and hydrogeological investigations are reported with additional new geochemical and isotopic data. Based on simulated groundwater flows from a numerical modeling of the field site and observed groundwater As concentrations, an As mass balance has been established for the Holocene aquifer.

2. Study site

2.1. Red River basin

The Dan Phuong field site is located in the central part of the Red River basin, close to the main river (Fig. 1), with a distance to the mountains surrounding the flood plain of approximately 10 km. The land use is dominated by non-irrigated crops, such as corn and sweet potato, which are harvested in June and December. The area is flat but with drainage of surface run-off and a near-surface interflow into channels running through the field site. The present position of the Red River on the flood plain is controlled by the dykes alongside the river (Fig. 1): these dykes were constructed approximately 1 ka ago.

The climate in the study area is dominated by the Southeast Asian monsoon system with a rainy season from May/June to October/November. The average discharge in the Red River is about 3700 m$^3$/s with recorded variations between 370 and 38,000 m$^3$/s (Ngo, 2006). The water stage at Sontay station varies between 6 and 12 m above sea level. During most years, the river stage at Sontay station varies between 6 and 12 m above sea level (Fig. 2). Ngo (2006) defines the pre-flooding season as the period with a fast increase in the river stage in May–June, the flooding takes place during July and August, and the post-flood season is from late August to October with a falling river stage. Upstream of the field site, there are two reservoirs, which have an impact on the river stage. The release of water from these reservoirs may cause abrupt increases in the river stage during periods with a low water level. The precipitation record at Sontay station, from 1993 to 2003, is depicted in Fig. 3a. The mean annual precipitation in this period was 1640 mm with 70% of the rain falling from May to October. During the monsoon the monthly rainfall exceeds 300 mm, the daily rainfall is typically between 10 and 50 mm/day but extreme events with up to 100–200 mm/day are recorded every year. The potential annual evaporation in northern Vietnam is typically 700–800 mm, and some years up to 1000 mm.

In this hydraulic regime, a hydraulic year can be considered as the period from the beginning of the pre-flooding in one calendar year (May/June) to the end of the dry season the following calendar year.

Fig. 2. Mean monthly water stages in the Red River from year 1990 to 2001, measured at Sontay, 16 km upstream of the field site. Error bars indicate ±1 standard deviation.

The Red River flood plain sediments consist of a Pleistocene and Holocene sequence of gravel, sand and clay deposits, with a thickness ranging from a few meters in the NW to 100–200 m at the coast, and are overlying Neogene deposits (Mathers and Zalasiewicz, 1999; Nielsen et al., 1999; Lam and Boyd, 2003; Tanabe et al., 2003a,b, 2006). During the Quaternary period, alluvial and fluvial sediments have been transported by braided rivers from the NW towards the SE, to the Gulf of Tonkin. The boundary between the fluvial dominated and shallow marine depositional environments has shifted during the Pleistocene and Holocene in response to eustatic sea level changes (Tanabe et al., 2003a). However, during the Quaternary the sea has never transgressed the flood plain as far inland as the present location of Hanoi (Tanabe et al., 2003a). Because the Dan Phuong field site is located NW of Hanoi, the aquifer sediments have been deposited by fluvial systems during the Pleistocene and Holocene. Initially the depositional environment must have been braided rivers, later followed by meandering river systems.

2.2. Dan Phuong field site

The thickness of the Pleistocene and Holocene deposits increases from the marginal mountains towards the central part of the flood plain, reaching a thickness of 60–70 m at Dan Phuong. The thickness of the Holocene aquifer increases from a few meters near the mountains to 30–35 m at the field site. The flat area between the mountains and the Red River is intersected by a dense network of channels, which are in hydraulic contact with the shallow Holocene aquifer.

At the Dan Phuong field site, the Red River forms a large meandering bend (Fig. 1) and the shallow sediments are characterized by sandy point bar systems and channel deposits of sand and gravel, overlain by clay-rich deposits with a thickness of up to 10 m. The confining clay-rich layer has been laid down as overbank deposits. The area between the Red River and the main dyke is intersected by two, approximately 30 m wide distributaries of the main river and these are, in the following text, referred to as the southern and northern channel (Fig. 1). The elevation of the bottom of these channels is approximately +6 m above sea level. During the rainy season, water flows through the two channels from the west towards the east, and the channels and the river are hydraulically connected. During the dry season, the two distributaries become isolated from the main river but they continue to interact.
with the shallow Holocene aquifer, controlled by the local head differences and hydraulic properties of the streambed sediments. At low river stages, the channel waters drain into the main river through constructed outlets towards the east.

The geology at Dan Phuong is depicted in a cross-section in Fig. 4. Holocene deposits are found from elevation +10 m and down to elevation from −25 m. Preliminary optical luminescence (OSL) dating of the Holocene aquifer sand, sampled 10 m below the surface, suggests a burial age of 460 ± 30 a. The island between the Red River and the northern channel is dominated by sandy deposits, overlain by a confining clay layer towards the east. In the area between the two channels, the thickness of the clayey overbank deposit is up to 8 m. Inspection of the confining layer in the channel bank deposits shows intensive fracturing of the upper, weathered layers. Underlying the confining layer are fine to medium grained fluvial sand deposits, with up to 1 m thick interbedded, discontinuous layers of clayey silt and fine sand. The sand contains disseminated fragments of organic material and the clay-rich layers have larger plant fragments and roots. In the southwesterly part of the field site (Fig. 4) there is an up to 4 m thick deposit of clay that forms an aquitard between the Holocene and Pleistocene sandy aquifers. This clay layer is not found in the northeasterly end of the field site, where the transition between the Pleistocene and the Holocene aquifer deposits is identified by a change in grain size of the fluvial

Fig. 3. (a) Mean monthly precipitation at Sontay station from 1990 to 2003. Error bars indicate ±1 standard deviation. (b) Measured δ¹⁸O values in Hanoi precipitation sampled from 2002 to 2007. (c) The relationship between δ¹⁸O and δD concentrations in precipitation through the years from 2002 to 2007.
sediments. In general, the coarser deposits are found in the Pleistocene fluvial system, and the lowermost 10–20 m of deposits are cobbles and boulders, probably laid down as alluvial fan sediments. The underlying Neogene deposits are located 50–60 m below the surface.

The depth of the Red River at the field site was measured by a lead from a boat. The river was found to be 13 m deep near the southern bank decreasing to only 2 m towards the northern bank (Fig. 4). This depth range indicates that the Red River channel near Dan Phuong has been eroded in the Holocene deposits. Hydraulic contact between the river and the Pleistocene aquifer may therefore only be conducted through the Holocene deposits.

3. Methods

3.1. Sampling of precipitation and surface water

Since 2002, precipitation has been collected at the roof of the Institute for Nuclear Science and Technology in Hanoi. Sampling is done in a standard device following recommendations given by IAEA (2002). Mixed monthly samples were pipetted into 100 mL vials for analysis of the stable isotopic composition ($\delta^D$ and $\delta^{18}O$) of the water.

Red River water samples have also been collected monthly since 2002 in the same location in Hanoi. At Dan Phuong, water samples from the Red River and the two channels have been collected since May 2005. The samples were collected at 1 m depth using a 500 mL glass bottle and were analyzed for $\delta^D$ and $\delta^{18}O$.

3.2. Instrumentation of field site

A total of 40 observation piezometers were installed in the Holocene sand to describe the overall groundwater flow. Two transects consisting of 100 piezometers (H-transect) and 56 piezometers (K-transect) were established. Two of the K-piezometers (K11 and K50) have screens in the upper layers of the Pleistocene aquifer. These transects have been used for hydraulic head measurements and groundwater sampling. The K-transect is oriented perpendicular to the southern channel, in a part of the aquifer with a relatively good hydraulic contact between the surface water and the shallow groundwater. The H-transect is oriented almost perpendicular to the northern channel, in an area with a poor direct hydraulic contact between the surface water and the shallow groundwater. The location of the two transects is shown in Figs. 1 and 4. The two transects are aligned almost parallel with the regional northeasterly groundwater flow direction towards the Red River.

The piezometers were installed using jet drilling, down to 22 m, and equipped with $\varnothing$ 64 mm PVC-casings, 0.3 m screens and 1 m sand traps. The positions of the screens are indicated by the crosses in Fig. 6. The water used for jet drilling was pumped from nearby boreholes or from the channels. A quartz sand filter pack was installed, and the well was sealed using bentonite. The top of the PVC casings at the well heads was sealed to prevent the entrance of surface water during flooding. Immediately upon completion, the well was pumped to remove the water affected by the drilling operation. Then the well was left at rest for at least 3 months before sampling.

For hydraulic characterization and water sampling, four 12” diameter boreholes were drilled with a bailer and equipped with 160 mm PVC pipes and 6 m long screens. The boreholes were drilled at the locations T1 and T2 (Fig. 1); two at each location with screens in either the Holocene or the Pleistocene aquifer.

3.3. Sediment and water sampling

Sediment sampling for optically stimulated luminescence (OSL) dating of the burial age (Murray and Oley,
1999) was done by coring of sediments 15 m below the surface in a borehole drilled close to the H10 piezometer in the H-transect. A steel coring device (0.5 m × ø 64 mm) was used for this sampling. The cores were sealed and stored in Al-laminate bags to prevent exposure to sunlight after sampling and in this state brought to Denmark. For hydraulic characterization of the sand in the unsaturated zone, an intact core from the base of the confining clay to the water table was collected adjacent to the H1 piezometer, in the H-transect, at the end of the dry season.

Field procedures for inorganic geochemistry sampling are summarized in Postma et al. (2007). Water for stable isotope analysis was sampled in 1 L glass bottles. Groundwater samples from the Holocene aquifer were collected from the two transects and from the Pleistocene from the boreholes T1 and T2 and from the K11 and K50 piezometers.

Samples for 3H/3He dating of the groundwater were taken from screens placed at different depths in the distance range from 64 to 75 m in the H-transect (Fig. 6). Water was sampled in 50 cm long sections of 3/8" (0.95 cm) diameter Cu tube sealed at either end with pinch-off clamps (Stute and Schlosser, 2000). Dissolved gas samples for noble gas analysis were collected in passive diffusion samples (Sanford et al., 1996) which were placed in the borehole for 24 h. The dissolved gas pressures in the borehole water were measured. Sampling of the H-transect was done in November 2005 and the K-transect was sampled in November 2006. Samples from the Pleistocene aquifer were taken from the T1 and T2 boreholes in November 2006 and 2007.

3.4. Estimation of hydraulic parameters

The transmissivity and storativity of the Holocene and Pleistocene aquifers were determined from pump testing of the T boreholes, using the Theis method for unsteady-state flow in confined aquifers. Horizontal hydraulic conductivities of the Holocene sand were estimated from slug tests performed in piezometers (Hvorslev, 1951) and from sieving analysis. Residual water content and sediment porosity were estimated on the intact core material from the unsaturated zone. Assuming that the unsaturated zone sands are fully drained by the end of the dry season, the specific yield of the unsaturated zone is determined as differences from a known water volume in the plastic bag in a given time (Lee, 1977).

In this paper, percolation is referring to the water flowing downwards from the root zone. The percolation can either reach the shallow aquifer as recharge or support a near surface lateral groundwater flow (interflow). At the field site, shallow drainage ditches have been established every 50–100 m to enable an efficient drainage of the arable land in the rainy season. Rainwater run-off to the ditches also occurs in periods of high-intensity rainfall.

3.5. Water level measurements

Water levels in boreholes and in the two channels have been measured manually bi-monthly since May 2005. Water level and atmospheric pressure variations have also been measured in boreholes and piezometers with the use of pressure transducers (Van Essen Instruments, Delft, The Netherlands). Recorded water pressures have been corrected for atmospheric pressure variations.

3.6. Laboratory water analysis procedures

Laboratory procedures used for inorganic analysis are summarized in Postma et al. (2007). The Noble Gas Laboratory at the University of Utah, Department of Geology and Geophysics analyzed the samples for 3H and dissolved gases. For further details, see e.g. Manning et al. (2005). Corrections were made for degassing effects, and ages of the water were interpreted by the laboratory. The luminescence dating of the sediment was done at the Nordic Laboratory for Luminescence Dating, Risø National Laboratory, Denmark. The stable isotopic composition of the water samples was analyzed at the Institute for Nuclear Science and Technology in Hanoi using a MicroMass Spectrometer (IsoPrime, GV Instruments, UK) equipped with an Eurovector elemental analyzer (EuroEA 3000, Italy). Data processing was performed using the Masslynx Program supplied by GV Instruments Com., UK. The isotopic composition of 2H and 18O is determined as

$$\delta D = \frac{R_{\text{sample}} - R_{\text{std}}}{R_{\text{std}}} \times 1000, \%$$

$$\delta^{18}O = \frac{R_{\text{sample}} - R_{\text{std}}}{R_{\text{std}}} \times 1000, \%$$

The results are given in %o δ-notations with reference to the VSMOW standard (Coplen, 1996) and have a precision better than 0.1%o for δ 18O and 1.5%o for δD.

3.7. Hydrogeological modeling

A transient numerical groundwater flow model was set up for the field site using the code MODFLOW (McDonald and Harbaugh, 2005). Analytical solutions of surface and groundwater interactions were solved using the software STW1 (Barlow and Moench, 1998).

4. Results

4.1. Local geology and hydrogeology

The spatial distribution of the thickness of the confining clay-rich layer between the two channels has been compiled from geophysical and drilling data (Fig. 5). The clay layer reaches a thickness of about 6 m in a central area between the two channels. It thins out towards the southern channel near the K-transect (Fig 5). In the banks of the southern channel, the thickness of the clay layer is only approximately 0.5 m. When the river is low, the Holocene aquifer sand outcrops in the bank of the channel, whereas during high water a direct hydraulic contact is established between the surface water and shallow groundwater.

In the southern part of the H-transect, the thickness of the confining mud layer is only 2–3 m (Fig. 5) and hand
drilling revealed the clay layer to be oxidized throughout. In the northern end of the H-transect, adjacent to the northern channel, the geophysical and drilling results showed a thickness of the confining clay layer of up to 8 m. North of the northern channel, the island is dominated by sandy deposits (Fig. 4) which are in direct hydraulic contact with the Holocene aquifer through the high permeable sands below the northern channel (Fig. 4). Therefore, when the hydraulic head is increasing in the channel and the Red River, the pressure can be transmitted to the shallow aquifer between the channels from the north.

Observations during drilling showed that the clay-rich superficial layer contains an upper oxidized zone and a lower reduced zone. Near surface clay-rich deposits commonly have an upper highly fractured oxidized zone overlying a reduced zone with fewer fractures (e.g. Cherry, 1989; Jørgensen and Fredericia, 1992; McKay et al., 1993; Jørgensen et al., 2002). At Dan Phuong, the thickness of the oxidized zone is typically 3–4 m. Oxidized zones are characterized by a high density of sub-vertical fractures, which often have a prominent staining from Fe-oxides and Mn-oxides and a matrix with a yellowish brown color due to the presence of Fe-oxides in the clay. Most of the fractures in the upper few meters are the result of desiccation during periods of low water table. The spacing between the fractures in the reduced zone is larger and the fracture apertures are generally smaller (Jørgensen et al., 2002).

4.2. Hydraulic parameters

For use as input parameters in the numerical groundwater flow model, the hydraulic parameters of the Pleistocene and Holocene aquifer sand and the channel bottom sediments have been estimated. The results are summarized in Table 1. The estimated transmissivity of the Holocene sand from the pump testing varies from 3.4 to 3.7 x 10⁻³ m²/s and the storativity varies from 1.0 to 1.6 x 10⁻⁴. The average hydraulic conductivity of the saturated Holocene sand (thickness 25 m) was calculated to be 1.4 x 10⁻⁴ m/s. The spatial distribution of the hydraulic conductivity in the K-transect from slug tests varies from 0.2 to 8 x 10⁻⁴ m/s (Fig. 6a), with an average hydraulic conductivity of 3.6 x 10⁻⁴ m/s. In the H-transect values vary between 0.3 and 16 x 10⁻⁴ m/s with an average value of 3.3 x 10⁻⁴ m/s (Fig. 6b). Weber et al. (1972) studied the spatial permeability distribution in Holocene fluvial channel-fill sediments, and their results are similar to those of the present study. Fluvial aquifers are typically built of fining-upwards cycles of sand, silt and clay up to 5–10 m thick (Gani and Alam, 2004), and the observed hydraulic heterogeneity in the studied aquifers will therefore be seen at this scale. The most permeable layers probably represent more coarse grained deposits laid down in point bars, while zones with a lower hydraulic conductivity likely to be more fine grained sand and silt representing channel fill deposits. The distance between highly permeable zones in the Dan Phuong resembles spatial variations reported by Gani and Alam (2004). The porosity of the well sorted sand from the Holocene is remarkable high with values ranging between 32% and 49% (average 39%). Tanabe et al. (2006) also observed a high porosity, up to 50%, in Holocene sandy sediments from the Red River delta flood plain.

The estimated transmissivity of the Pleistocene sand is from 2.2 to 4.4 x 10⁻³ m²/s and the storativity is between 1.5 and 6.0 x 10⁻⁴. Hydraulic conductances of the bottom sediments in the channels, ranging from 0.04 to 1.10 m²/day (average 0.3 m²/day), were calculated from seepage meter measurements, using a channel width of 30 m and a thickness of the bottom sediments of 4 m. The measured water retention in the unsaturated profile ranged from 0.41 in the capillary fringe to an almost constant value of 0.08 further upward. The thickness of the capillary fringe in the fine to medium grained sand was 0.8 m. The estimated specific yield varied from 0.04 in the capillary fringe to 0.31 in the upper part of the unsaturated sand (average values of 0.2).

4.3. Seasonal dynamics in the Holocene aquifer

The elevation of the water table in boreholes and channels during the dry season is between +6.2 m in the SW to +5.2 m in the NE (Fig. 7a). In the dry season the groundwater table is lower than the bottom of the channels and leakage will occur into the aquifer through low permeability, bottom sediments. During this time of year a high hydraulic gradient builds up towards the Red River amounting to approximately 1.3‰, and in this part of the aquifer the direction is towards the NE (45–50° NE). Using the average hydraulic conductivity for the Holocene sand of 3.5 x 10⁻⁴ m/s, and an average porosity of 39%, the calculated horizontal Darcian and particle velocities in the dry season are 14 m/a and 37 m/a, respectively. Because there is no upward flow to the channels in the dry season, the groundwater flow between the two channels can, at a first approximation, be conceptualized using a simple flow...
model with uniformly increasing age of the water with increasing depth (Vogel, 1967). Based on $^3$H/$^3$He dating of the groundwater, an average vertical groundwater particle velocity of 0.5 m/a was determined in the H-transect by Postma et al. (2007). Again, using an average porosity of the sand of 0.39, this vertical particle velocity corresponds to a total, average recharge rate from both surface water and percolation of 195 mm/a. This recharge rate represents the hydrogeological conditions below the covering clay between the two channels, and higher recharge probably takes place in the sandy area north of the northern channel.

Table 1
Estimated hydraulic properties

<table>
<thead>
<tr>
<th>Type</th>
<th>Transmissivity range (m²/s)</th>
<th>Storativity range</th>
<th>Hydraulic conductivity range/average (m/s)</th>
<th>Porosity range/average (%)</th>
<th>Specific retention range/average</th>
<th>Specific yield range/average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pleistocene sand</td>
<td>$2.2 \times 10^{-3}$ to $4.4 \times 10^{-3}$</td>
<td>$1.5 \times 10^{-4}$ to $6.0 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-4}$ to $1.6 \times 10^{-4}$</td>
<td>$0.2 \times 10^{-4}$ to $3.5 \times 10^{-4}$</td>
<td>$32$ to $49$</td>
<td>$0.08$ to $0.41$</td>
</tr>
<tr>
<td>Holocene sand</td>
<td>$3.4 \times 10^{-3}$ to $3.7 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-4}$ to $1.6 \times 10^{-4}$</td>
<td>$2.0 \times 10^{-4}$ to $3.5 \times 10^{-4}$</td>
<td>$2.0 \times 10^{-4}$ to $3.5 \times 10^{-4}$</td>
<td>$32$ to $49$</td>
<td>$0.08$ to $0.41$</td>
</tr>
</tbody>
</table>

Fig. 6. Results from the K-transect and the H-transect. Crosses indicate sampling points and contouring is based on a measurement at each sampling point (vertical anisotropy factor 3); (a,b) Hydraulic conductivities of the Holocene aquifer sand based on results from slug tests; (c,d) $\delta^{18}O$ of groundwater from the transects; (e,f) Groundwater As concentrations in the Holocene aquifer in the two transects.
The groundwater head distribution during the monsoon is shown in Fig. 7b. The water table is now virtually flat with elevations varying between +8.38 m and +8.28 m. The previous northeasterly flow has been stalled by the increasing stage in the Red River.

Fig. 7c illustrates the interaction between the water in the channels and the aquifer by comparing the hydraulic heads in the southern channel and borehole (C9) located 170 m north of the southern channel (Fig. 1). During the pre-flooding period of June 2005, the water stage in the channel increased rapidly and a steep gradient was established towards the aquifer. Therefore surface water flows into the aquifer where the bank sediments are permeable. From July to October the water stage in the channel varies drastically and it is controlled by the release of water from the reservoirs upstream of the field site. The result is a succession of gaining and losing phases at the interface with the aquifer. During the post-flooding period, from October to November, the water stage in the channel decreases drastically and groundwater flows towards the channel for some months. The increase of the water stage in the channel during January–February 2006 (Fig. 7c) is probably again due to the release of water from the upstream reservoirs. The groundwater table remains above the groundwater table. From June to August 2006, the water table increased from an elevation +5.80 m to +8.43 m (data not shown). Using an average specific yield of the Holocene sand of 0.2 (Table 1), this corresponds to an uptake of water of 0.53 m³/m² of the aquifer.

In the southern part of the field site, recharge of surface water from the southern channel into the shallow aquifer built up higher hydraulic heads in the Holocene than in the Pleistocene aquifer through most of the year. The downward flow of groundwater from the Holocene to the Pleistocene aquifer mainly occurs north of the area where the aquitard is present. Further towards the north, where the aquitard is absent, upward hydraulic gradients from the Holocene to the Pleistocene are observed, and consequently this area is a discharge zone with groundwater flowing upward from the Pleistocene deposits into the Holocene and further into the Red River.

4.4. Isotopic and chemical composition of precipitation in Hanoi

The concentrations of $^2$H and $^{18}$O in meteoric waters, which have not undergone extensive evaporation, will show a linear correlation (Craig, 1961). For precipitation in Hanoi this relationship is given by the equation $\delta^2H = 8.3 \times \delta^{18}O + 13.5$ (Fig. 3b). The annual distribution of $\delta^{18}$O in precipitation from Hanoi (Fig. 3c) shows an enrichment in the dry season from October to May with $\delta^{18}$O values typically between 0‰ and −4‰, while during the rainy season, depletion of rain is seen and $\delta^{18}$O varies between −8‰ and −14‰. These seasonal trends of $\delta^{18}$O in rainwater are similar to those previously described from the Asian South Pacific by Dansgaard (1964), Lawrence and White (1991), Rozanski et al. (1993) and Araguás-Araguás et al. (1998). The phenomenon is known as the amount effect, and it is due to secondary evaporation, causing $^{18}$O enrichment, during rainfall in the dry season (Friedman et al., 1962; Dansgaard, 1964; Clark and Fritz, 1997).
During monsoon rainfalls the relative humidity of the air is close to saturation and secondary evaporation does not occur. Araguás-Araguás et al. (1998) showed that the amount effect has an impact on the stable isotopic composition of the precipitation at a distance of up to 700 km from the Southern Pacific coast. In the Red River flood plain, the amount effect provides a characteristic seasonal isotopic fingerprint on the precipitation.

4.5. Stable isotopic composition of surface and groundwater

The variations of \( \delta^{18}O \) in the Red River water samples during 2006 are depicted in Fig. 8 and the values range between \(-11\%e\) and \(-7\%e\). During the dry season, \( \delta^{18}O \) values in the river water are between \(-9\%e\) and \(-7\%e\), but after the monsoon rain, the Red River water becomes more \( ^{18}O \) depleted with \( \delta^{18}O \) values in the range \(-11\%e\) and \(-9\%e\). In the northern channel the \( \delta^{18}O \) values range between \(-6\%e\) and \(-9\%e\) in the dry season (Fig. 8), whereas in the rainy season the channel and the Red River become connected and yield the same the \( \delta^{18}O \) values. Enrichment of \( ^{18}O \) in the channel water during spring is the combined effect of evaporation of water in the channels and \( ^{18}O \) enriched spring precipitation (Fig. 3c).

The spatial distribution of \( \delta^{18}O \) in the K-transect on November 2006 is displayed in Fig. 6c. Note that the southern end of the K-transect is adjacent to the bank of the southern channel (Fig. 1). The \( \delta^{18}O \) varies between \(-9\%e\) and \(-4\%e\), with maximum values between \(-5\%e\) and \(-4\%e\) clustered in a zone approximately 10 m from the southern channel. Values between \(-7.5\%e\) and \(-6.5\%e\) are found where the clay layer is thin at distances up to 40 m from the southern channel. When the clay layer becomes thicker the \( \delta^{18}O \) values only vary between \(-9\%e\) and \(-7.5\%e\). The \( \delta^{18}O \) composition of the water in the H-transect is displayed in Fig. 6d. The \( \delta^{18}O \) values in the H-transect are confined to a narrow range between \(-10\%e\) and \(-8\%e\). There is no clear pattern in the spatial distribution of \( \delta^{18}O \) as was seen in the K-transect. The differences in \( \delta^{18}O \) distribution between the K and H transects are interpreted as follows: The zone in the K-transect with \( \delta^{18}O \) values of \(-5\) to \(-4\%e\) reflects surface water that has recharged to the aquifer during July–August, 2006. In the 3–4 months that passed until sampling in November 2006, the surface water has moved approximately 10 m horizontally into the shallow aquifer. The intermediate values between \(-7.5\%e\) and \(-6.5\%e\), below the thin clay cover, are most likely due to an input of surface water infiltrated through the clay cover during the flooding. The isotopic composition of the water below the thicker clay resembles the values in the H-transect, and this water was most likely recharged by percolation through the covering clay layer. The limited variation in the \( \delta^{18}O \) values in the H-transect indicates that in this part of the aquifer, the surface water is not flowing from the channel into the aquifer during high river stages. This conclusion is consistent with the presence of a thick clayey deposit just south of the northern channel (Fig. 5), and the chemical composition of the water in the northern part of this transect (Postma et al., 2007). The groundwater \( \delta^{18}O \) composition in the H-transect resembles that of precipitation in Hanoi during the rainy season (Fig. 3c). Apparently recharge to the Holocene aquifer near the H-transect predominantly proceeds by percolation through the covering clay layer during heavy rainfall in the monsoon period.

Groundwater concentrations of Cl− and \( \delta^{18}O \) compositions of water from the two transects are shown in Fig. 9. The increase in Cl− concentration from precipitation to recharge water in the H-transect is not reflected in increasing \( \delta^{18}O \) values, indicating that evapotranspiration is the main mechanism for water loss, since this is a non-fractionating process (Zimmerman et al., 1967; Förstel, 1982). Water is also taken up by the fast growing bio-mass (mainly corn) and this is also a non-fractionating process with probably little uptake of Cl− from the water. In contrast, the southern part of the K-transect shows high \( \delta^{18}O \) values associated with a high concentration of Cl− (Fig. 9). In this case, the \( \delta^{18}O \) and the Cl− content of the water appear to be controlled by evaporation from a free water surface in the channel or from the top soils. The recharge of surface water to the aquifer can be delineated as the zone with low \( \delta^{18}O \) enrichment (Fig. 6c).

The stable isotope composition of the water in the Pleistocene aquifer is more depleted than the groundwater.
from the Holocene aquifer with $\delta^{18}$O values between 
$-11\%$ and $-10\%$ and $\delta^2$H values between $-67\%$ and $-66\%$ (Table 2). The higher depletion with respect to heavy O and H isotopes of the water in the deeper, Pleistocene aquifer most probably reflects the influence of recharge water precipitated at higher elevations in the mountains around the flood plain.

4.6. Groundwater flow modelling

To quantify recharge and surface–groundwater interaction, a transient numerical groundwater model was set up for the model area depicted in Fig. 1, using the hydraulic data listed in Table 1. Towards the north, the model uses a general head condition as boundary condition, based on linearly interpolated daily measurements at the stations in Son lay and Hanoi. The eastern and western boundaries of the model area are considered as no flow boundaries. The seasonally changing flow conditions in the Holocene aquifer raises the question of the appropriate position of the southern flow boundary. This boundary should be placed far enough from the southern channel to maintain north-moving flow throughout the year. In the southern part of the model domain the saturated total thickness of the Pleistocene and Holocene aquifers is approximately 45 m (Fig. 4) and the boundary length is 5000 m (Fig. 1). Head measurements in boreholes C18, C19, C20 and C21, located approximately 500 m south of the southern channel (Fig. 1), show that during 11 months of the year, the water table has a slope towards the north with a hydraulic gradient between 0.5% and 1%. Using an average hydraulic conductivity of $3.5 \times 10^{-4}$ m/s for the aquifer sand, the estimated annual flux across the southern boundary is between 1.2 and 2.4 million m$^3$.

During high water stands in the Red River and the channels (middle of June to middle of July), the hydraulic gradient at boreholes C18–C21 is reversed and the groundwater flows towards the south. Southward groundwater flow during this reversed flow period amounts to approximately 5% of the northward groundwater flow during the remaining 11 months of the year. Based on a regional catchment model, Chambon (2007) estimated a groundwater flow of approximately the same magnitude along the south-southwest facing boundary. An analytical solution for a confined aquifer with an initial gradient of 1% towards the north, solved using the code of Barlow and Moench (1998), shows that the observed change in the water level of the southern channel should reverse the hydraulic gradient towards the south to a distance of up to 1500 m from the channel. Therefore in the numerical model the southern boundary is placed at 2500 m from the southern channel. At this boundary a variable flux of 5000 m$^3$/d was used, except in August when the hydraulic gradient is lower and the flux was reduced to 1250 m$^3$/d.

The channels running through the field site were modeled using the MODFLOW River Package. Transient channel stages, required as model input, were compiled from (i) hand measurements in the channels, (ii) the Red River stage time series and (iii) daily pressure transducer recordings from the rainy season in 2007 in the northern channel. During the dry season, the channel stages are above the stage of the Red River (i.e., a perched water table), whilst in the wet season, the water from the Red River main channel flows through the channel distributaries and the stage variations become identical. This head dependent surface water–groundwater interaction is built into the model.

As described in Section 4.5 recharge from percolation occurs mainly during the rainy season, and therefore in the model recharge could be confined to these months. To be able to reflect the variations in the rainfall during the monsoon, an input time series for recharge to the aquifer was calculated as a fraction of the daily precipitation record from the Son lay station. The recharge/precipitation fraction was calculated using a 10-a record, in order to comprise the influence of year-to-year variations in precipitation on the recharge rate. As the model aimed at establishing an overall water balance for the study site, the recharge rate time series was applied uniformly over the model domain. Conductance constants for the bottom sediment of the Red River and the channels were set to 4.0 and 0.5 m$^2$/day, respectively. The higher conductance of the Red River reflects that the bottom sediments of the river are more coarse grained than the channel sediments (Fig. 4). The specific yield of the sand is 0.2 (Table 1) and is set to 0.015 in the confining clay. In order to simulate the dynamics in head and fluxes satisfactorily, short stress periods of one to two days were used along with the daily input data for recharge, Red River and channel stages in the rainy season, whereas the dry season stress periods were up to 31 days.

The model calibration was done using observation data from 15 May 2005 to 14 May 2006 and validated against observation data from 15 May 2006 to 31 December 2006 (i.e., the rain season of 2006). In the calibration process, the parameters, (i) flow across the southern boundary; (ii) the recharge rate; (iii) the conductance of Red River and channels; and (iv) the specific yield of the confining clay-rich layer, were changed manually within reasonable values to improve the match between observed and simulated values.

Sensitivity analysis on these parameters was done by reducing and increasing the calibrated values by a factor of 2. The model was relatively insensitive to the value of the conductance of the Red River bed, with head off-sets of approximately ±0.05 m relative to the calibrated model. The value of the specific yield of the confining clay had a high impact on the simulation of the hydraulic head peaks during the surface water stage extremes. Poor fits were obtained for the rainy season if this value was outside the range 0.010 to 0.025. The highest sensitivities, with head off-sets on the order of ±1 m, were found for the recharge,
and the channel bed conductance, and not surprisingly the flow across the southern boundary. The latter model uncertainty was reduced by carefully sampling the head observations along this boundary and the uncertainty has therefore been confined to the estimated hydraulic conductivity of the sand, which seems well documented. The estimated conductance of the channel appears high and could very well be wrong by a factor of 5–10. Mean error (ME) values between simulated and observed hydraulic heads, using a uniform recharge rate of 60 mm/a, is 0.57 m in the calibrated model and 0.60 m in the validated model. Increasing the recharge rate gave larger errors and with a recharge rate of 100 mm/a, the ME values of the calibrated and validated model increased to 0.77 m and 0.80 m, respectively. The mean absolute errors (MAE) in the validated model with a recharge of 60 and 100 mm/a were 0.78 and 0.93 m, respectively. Given the above mentioned uncertainties in the flux across the southern boundary and the conductance of the channels, the uncertainty on the calibrated recharge rate alone from percolation could work equally well with a percolation of 100 mm/a. Increasing the recharge rate to much more than 100 mm/a is not possible with the calibrated flow model without simulating unrealistically high hydraulic heads.

The observed and simulated hydraulic heads in boreholes C2, C5, C9 and C19 are depicted in Fig. 10 and show that when the water table rises, the simulated hydraulic heads match the observed values very closely, generally with differences smaller than 0.1 m. The larger deviations between observed and simulated heads during peaks are due to variations in the specific yield of the confining clay layer. When the water table falls, the model generally simulates the high head values correctly in the beginning but later the modeled water table becomes too low, with deviations up to 0.6 m. This mismatch is probably caused by a

![Fig. 10.](image-url) (a–d) Observed and simulated groundwater heads in boreholes. (e) Observed and simulated hydraulic gradients between the K50 and H50 boreholes located within a distance of 750 m in the two transects.
delayed yield from the fine grained sand during falling water conditions. Simulated and observed hydraulic gradients between boreholes K50 and H50, located 750 m apart, are also shown in Fig. 10. The simulated hydraulic gradient shows differences between the observed and measured hydraulic gradient of less than 0.2‰, and therefore the overall dynamics of the system appear to be well described by the model.

A water budget for the model area, based on groundwater flow calculated with the validated model, is depicted in Fig. 11. The simulated groundwater flow from May 2005 to May 2006 across the southern boundary is 1.6 million m$^3$. This is distributed between the Holocene and Pleistocene aquifers with 0.9 and 0.7 million m$^3$, respectively. The southern and northern channels together recharge 1.6 million m$^3$ into the aquifer, mainly during the rain season. In the months after the rain season 0.6 million m$^3$ of groundwater is discharged back into the two channels, with a higher flux flowing into the northern channel due to the higher hydraulic head in this part of the aquifer. Using a uniform recharge rate of 60 mm/a, the total annual recharge from percolation is 1.4 million m$^3$, about the same amount as the recharge from the channels (1.6 million m$^3$). Where the separating aquitard clay layer between the aquifers is not present, 2.4 million m$^3$ flows downward into the Pleistocene aquifer, mainly in the upper few meter of this aquifer. During the simulated year, 4.7 million m$^3$ groundwater discharged into the Red River, and 1.2 million m$^3$ flows back as bank infiltration during the flooding period. Water discharging from the Pleistocene into the Red River must flow up through the Holocene deposits, below the Red River. The storage change in the Holocene aquifer in the simulated year was 2.9 and +0.5 million m$^3$. Particle tracking simulation gives annually averaged hydraulic gradients between the two channels of 0.8‰ and horizontal particle velocities of 25–28 m/a. As expected this is smaller than the particle velocity of 37 m/a calculated from Darcy’s law and the high hydraulic gradient measured in the dry season (Section 4.3).

### 4.7. As concentration in groundwater

The groundwater in the Holocene aquifer is a CaHCO$_3$-MgHCO$_3$ type of water, mostly anoxic and enriched in CH$_4$ and Fe(II) (Postma et al., 2007). Fig. 6e and f shows the distribution of groundwater As in the two transects. At the southern end of the H-transect, the covering clay-rich layer is thin and the upper 2 m of the saturated zone contains dissolved O$_2$ and NO$_3$ (Postma et al., 2007, Fig. 4). This oxic zone contains less groundwater As than the detection limit of 0.013 μM As (1 μg/L). Below the oxic zone the total As concentration gradually increases, reaching values as high as 7.4 μM (555 μg/L). In the anoxic zone the degradation of organic material is the controlling process and As is released to the groundwater in association with the reduction of Fe-oxides. A more detailed discussion of the geochemical processes controlling the distribution of As in the aquifer is given in Postma et al. (2007). In the H-transect, the groundwater As concentration of 555 μg/L builds up along a downward gradient of 20 m corresponding to a groundwater age of 40 a (Postma et al., 2007). This is equivalent to an As release rate from the sediments of 14 μg/L/a. For comparison, Stute et al. (2007) reported an As release rate of 19 μg/L/a (with a range from 7 to 27 μg/L/a) in their study of a shallow aquifer system in Bangladesh.

The distribution of As in the groundwater of the K-transect (Fig. 6e) shows As to be present throughout the aquifer reaching a concentration of up to 6.6 μM (495 μg/L). Apparently the recharge water from the southern channel becomes quickly reduced and As seems to become mobilized already at the interface between the surface and groundwater, maybe in the bottom sediments of the channel. Polizzotto et al. (2006) in their study from Cambodia also observed mobilization of As near surface channel sediments.

The Pleistocene aquifer at Dan Phuong has only been sampled from a few boreholes in the T1 and T2 (for location, see Fig. 1) which are equipped with 6 m long screens,
and from the piezometers K11 and K50 in the K-transect. Samples from November 2006 (Table 2) showed As concentrations in the range from 1.4 to 3.9 μM (106–294 μg/L), and similar concentrations were found in samples from November 2007 (data not shown).

5. Discussion

One of the puzzling questions which still remain to be answered is why such large spatial variations in groundwater As concentration are observed both over large and small scales (e.g. Smedley and Kinniburgh, 2002; van Geen et al., 2003; Harvey et al., 2006). The results of this study indicate that the spatial distribution of As in groundwater of the Holocene aquifer is strongly affected by the hydraulic properties of the covering clay layer, through a control of the recharge rate, and the chemical composition of the water percolating through the confining clay layer.

5.1. The recharge mechanism of the Holocene aquifer

According to the numerical groundwater model, the annual recharge rates from percolation and from the two channels are of the same order in the model area: 1.6 and 1.4 million m³, respectively. Recharge rates show large variations due to the spatial variability of the top soil composition (clay or sand), the land use, topography etc. Based on ³H/³He profiles, Stute et al. (2007) report from Bangladesh a 10-fold range of recharge rates from 100 to 1100 mm/a and these findings suggest that a clear distinction must be made between areas with sandy and clay-rich deposits. The hydraulic properties of clay-rich near surface deposits were reviewed by Cherry (1989) and detailed field studies have been reported by McKay et al. (1993). The results from these studies reveal that the bulk hydraulic conductivity in oxidized zones of clay-rich deposits are typically 1–3 orders of magnitude larger than in the reduced zone, and therefore, surface near lateral groundwater flow (interflow) is often generated in the transition zone between the oxidized and reduced zones. At Dan Phuong, interflow occurs during the monsoon rainfall, and follows the hydraulic gradients towards the shallow drainage ditches, established for every 50–100 m in the arable land. A surface run-off of the monsoon rain also occurs and these processes together strongly reduce the recharge to the shallow aquifer in the area with clay-rich top soils. In areas with sandy top soils, the near surface water flow is vertical downwards and relatively fast water flow will probably also reduce the evapotranspiration, and higher recharge rates are therefore to be expected.

From the ³H/³He profile in the shallow Holocene sand, published by Postma et al. (2007), a total recharge rate of around 195 mm/a below the confining clay can be estimated. In addition, the results from the numerical modeling show that an average recharge rate from percolation much higher than 100 mm/a seems unlikely in areas covered by confining clay units.

At Dan Phuong, the interaction between surface water and the Holocene aquifer is highly dependent on the water stage in the channels, as the hydraulic conductivity of the clay-rich bottom sediments is much lower than that of the sandy sediments in the banks of the channels. To quote Woessner (2000): “The exchange of surface water with shallow aquifers in fluvial plain sediments is controlled by: (i) the distribution and magnitude of the hydraulic conductivity both within the channel bed and in the associated fluvial plain sediments; (ii) the relation of the channel stage to the adjacent groundwater gradients; and (iii) the geometry and position of the stream/channel within the fluvial plain”.

5.2. Chemistry of the recharge water

Electron acceptors (O₂, NO₃ and SO₄²⁻) are transported into the aquifer where the confining clay is less than 2–3 m thick. An approximately 2 m thick oxic zone, with a low As concentration, has developed in the underlying saturated Holocene sand. Over depth the As concentration increases and reaches a concentration of 7.4 μM As (555 μg/L) at 20 m depth. The transport of O₂, NO₃ and SO₄²⁻ through the covering clay will be controlled by the thickness of the clay, the capacity of the clay to reduce O₂ and NO₃, the water residence time in the layer, and diffusion into the clay matrix between fractures (Cherry, 1989; Jørgensen et al., 2002). When the thickness of the confining clay layer exceeds about 3 m, its base remains saturated and reduced most of the year, and electron acceptors are not transported into the aquifer. Here Fe-oxide reduction takes place from the water table and also the As concentration starts to increase (Fig. 6e and f). The average As mobilization rate is around 14 μg/L/a (Section 4.7) and the rate controlling chemical process is apparently the rate of sedimentary organic matter degradation (Postma et al., 2007). The groundwater As concentration is then the product of the water particle velocity and the As release rate from the sediments. Therefore local hydrogeological conditions will have a strong effect on the As concentration build up in the shallow aquifers.

The biogeochemical processes occurring in the hyporheic zone, the upper few centimeters of sediment below a surface water body, may have a profound effect on chemistry of interacting water (e.g. Brunke and Gonser, 1997; Dahm et al., 1998; Sophocleous, 2002). The composition of the groundwater in the K-transect (Fig. 6e) represents the situation 4 months after recharge from the southern channel. Yet the water contains no dissolved O₂, NO₃ or SO₄²⁻ and these components must have been reduced in the channel bottom or aquifer sediments. Massmann et al. (2004) described a case where river water infiltrates into a glacial fluvial aquifer and where dissolved O₂ and NO₃ already became reduced only a few meters into the stream bank. Whether in the present case As is mobilized in the bottom sediments of the channels is at present not known.

5.3. A mass balance for As in the groundwater

The Dan Phuong field site is located between the Red River and the dyke, and the sediments are therefore young, probably less than 500 a. Postma et al. (2007) suggested
that the situation in Dan Phuong could be viewed as a kind of initial state of the older sediments (up to 10 ka BP) in Bangladesh and W. Bengal (Goodbred and Kuehl, 2000). In this perspective it is useful to construct a mass balance for As for the Dan Phuong field site. The flux of groundwater As into the area can be calculated from the calculated flow into the model domain multiplied by observed average groundwater As concentrations. The estimated fluxes in the As mass balance are shown in Fig. 12. The average As concentrations of groundwater flowing into the Holocene and Pleistocene aquifers from the southern boundary have been set at 4 µM (300 µg/L) and 2 µM (150 µg/L), respectively, and with the regional groundwater flow 375 kg/a As enters the model area. The water recharging the Holocene aquifer from the channels will gain As either by mobilization within the aquifer or in the bottom sediments of the channel (Polizzotto et al., 2006) but there is no net flux of As entering the system this way. The groundwater flowing into the upper layers of the Pleistocene aquifer contains 720 kg As, assuming groundwater As concentrations of 4 µM, as seen in the bottom of the Holocene aquifer (Fig. 6e and f). Lower groundwater As concentrations in the Pleistocene suggest that at least some of this As is sorbed to the sediments in the Pleistocene aquifer. The mass of As leached into the Red River with the groundwater is around 945 kg/a, with 480 kg/a coming from the Holocene aquifer and 465 kg/a from the Pleistocene aquifer. In addition, 180 kg/a is transported with the groundwater into the channels after the monsoon period. The total amount of As leached from the Holocene aquifer is 1100 kg/a. The average As concentration in the sediment is 7.5 µg/g (Postma et al., 2007) and the total mass of As in the 24 km² model area is therefore 13.3 million kg As. The amount of As leached annually therefore corresponds to 0.01% of the total As mass in the Holocene sand.

There are considerable uncertainties in the constructed As mass balance but the main conclusions are quite clear. First of all, a considerable mass of As is transported annually from the aquifers to the Red River. Since the river water contains very low concentrations of dissolved As, the groundwater As is apparently precipitated together with Fe-oxides and incorporated in the sediments. In the long term this constitutes an As recycling loop since the As enriched sediment with time will be redeposited along the river and form a new aquifer.

The second main conclusion is that the amount of As exported from the system is small compared to the pool of As present in the sediment and a timescale of thousands of years is envisaged before the Holocene sediments become depleted in As which is in agreement with the estimates of Postma et al. (2007) based on the As release rate. The present rates of organic matter decomposition and thereby of As release must decrease over time (Postma et al., 2007) as the most reactive organic C becomes consumed and therefore the time required to deplete the sediment for As is a minimum estimate.

6. Conclusions

1. The flood plain aquifers at Dan Phuong show during the dry season (October to May/June) a regional groundwater flow directed towards the Red River, with horizontal particle velocities up to 37 m/a. In this period, the water stage of the Red River distributaries is typically above the groundwater table and recharge of the shallow aquifer occurs by leakage through the low permeable bottom sediments.

2. During the monsoon, the water stages in the Red River and its distributaries increases up to 6–8 m. This increase is stalling the regional groundwater flow in the adjacent aquifer and the result is a pattern of rapid fluctuations in groundwater table elevations and flow direction. During this phase, the groundwater tables increases up to 4 m within 2–3 months. Rapid fluctuations in the stages of the river and channels are generating a succession of gaining and losing phases at the interface with the aquifer.

![Fig. 12. A mass balance of As in the Holocene aquifer. Groundwater flows are simulated values from the numerical modeling and groundwater As concentrations are average observed concentrations in the Holocene and Pleistocene aquifers.](image-url)
3. Numerical modeling of the groundwater flow shows that recharge of the Holocene aquifer by surface water from Red River distributaries and from rainwater through a confining clay-rich layer are of the same order, being approximately 1.5 million m$^3$/a in the modeled area. An average areal recharge rate from percolation of 60–100 mm/a through the confining clay was obtained from the transient groundwater flow model, while a total recharge rate of 195 mm/a below confining clay layers was estimated from $^{3}$H/$^{3}$He dating of the water.

4. At places where the confining, clay-rich layer is less than 2–3 m thick, water containing electron acceptors ($O_2$, $NO_3$, and $SO_4^{2-}$) is transported into the aquifer through fractures, or sandy outcrops, and influences the redox conditions in the underlying aquifer. The spatial variation in the $As$ content of the groundwater becomes, accordingly, a function of the hydrogeological setting.

5. Arsenic is mobilized in the Holocene aquifer at a rate of about 14 g/L/a, possibly with retardation in the Pleistocene aquifer. An $As$ mass balance for the field site shows that around 1100 kg of $As$ is in this years annually leached from the Holocene sand and discharged into the Red River, corresponding to 0.01% of the total pool of $As$ present in the Holocene sand.

6. Variations in stable isotope composition of precipitation, surface water and groundwater have proved to be a useful tool in tracing surface–groundwater interactions in the shallow Holocene aquifer. This is mainly due to the amount effect in the precipitation which in parts of Southeast Asia offers a distinct seasonal isotopic signature, which can be traced in the hydrological cycle. In the studied site, groundwater from the Pleistocene aquifer is more depleted than water from the Holocene aquifer, probably reflecting a component of recharge water from the surrounding mountains of the Red River flood plain.

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