# Groundwater arsenic in the Red River delta, Vietnam

## Regional distribution, release, mobility and mitigation options

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Technical University of Denmark

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**PhD Thesis**
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# Abstract

Geogenic arsenic (As) in drinking water derived from groundwater is a threat to the health of millions of people living in South East Asia. In the Red Rive delta, Vietnam, alone, 10 millions of people are estimated to be at risk of developing serious and ultimately deadly diseases due to poisoning by As in their drinking water.

The content of As in groundwater in the Red River delta shows a distinct regional distribution, as shown by regional surveys by UNICEF and the Swiss EAWAG. As a part of this PhD thesis, the geological control on the groundwater As distribution was investigated, based on groundwater samples and geophysical logs collected along a 50 km transect across the southern and central part of the Red River delta. In the southwest part of the transect, Holocene, darkgrey-coloured estuarine clays and deltaic sands comprise most of the Quaternary sequence of 70 m. In the northeast end of the transect, Pleistocene, grey-yellowish alluvial sands and estuarine clays dominate the Quaternary sequence, which here thickens to 150 m. Elevated concentrations of dissolved $Fe^{2+}$, $HS^-$, $NH_4^+$ and $CH_4$, and absence of $SO_4^{2-}$, were observed in the Holocene deposits, relative to the concentrations in the Pleistocene deposits, where, in addition, $SO_4^{2-}$ was present. Apparently, the Holocene deposits were strongly reducing, compared to the Pleistocene deposits. The distribution of groundwater As appeared to be controlled by the redox environment, with concentrations up to 900 μg/L in the southern part of the transect, and lower As concentrations, <25 μg/L, in the northeast end of the transect. The distribution of groundwater As in the transect could be related to the palaeo-hydrogeology of the Red River delta. In Late Pleistocene, global cooling caused a low eustatic sea-level and the palaeo-Red River then eroded an incised valley along the southern boundary of the delta. The existing Pleistocene sediments adjacent to the incised valley became oxidized due to a deep groundwater table, and flushing by oxidizing groundwater at the then prevailing increased hydraulic gradients. During the sea-level rise in Holocene, a rapid deposition of sediments took place in the incised valley. The southwest end of the transect intersects the Holocene incised valley fills, which contain groundwater with a high concentration of As. The northeast end of the transect intersects the oxidized Pleistocene deposits generally low in groundwater As. Here, iron oxides and a decreased reactivity of the residual

organic matter may prevent As mobilization, and, in addition, As may have been flushed by the groundwater flow during the Late Pleistocene.

The hydrological and geochemical processes controlling the occurrence of As in groundwater of the Holocene aquifer were studied at a field site located on a point bar near the Dan Phuong village, 30 km upstream the Red River from Hanoi. Sediments from the river bed and adjacent aquifer contained microcrystalline goethite and subordinary amounts of hematite, as identified by Mössbauer spectroscopy. Arsenic and Fe(II) were concomitantly released when Fe(III) in the sediments was microbially reduced by natural organic matter or acetate in sediment incubations, or abiotically reduced by ascorbic acid in kinetic sediment extractions. The sequence by which As and Fe was released in the incubations, and the redox state of the released As, could be related to the redox potential of the $Fe(OH)_3/Fe^{2+}$ couple relative to that of the As(V)/As(III) couple. The thermodynamic analysis indicated that As is initially present as As(V) in the iron oxides, and is reduced to As(III) when As(V) becomes surface-exposed during the reductive dissolution of the iron oxides. The results are consistent with the current paradigm for the widespread groundwater As contamination in other South East Asian deltas. This paradigm prescribes that As is associated to iron oxides and become released upon their reductive dissolution and As(V) reduction, both microbially mediated and driven by organic carbon oxidation.

At the Dan Phuong field site, As released in the channel bed sediments was transported down gradient with the groundwater flow to the reduced aquifer, indicating a significant mobility of As in the reduced aquifer. A laboratory experiment with sediment from the reduced aquifer showed that adsorption of As(III) conformed to a strongly non-linear isotherm below an aqueous As concentration of about 100 μg/L. At an As concentration above 1 μM, the isotherm gradually approaches a sorption capacity of ca. 1 μg As per g sediment at an aqueous As concentration of 250 μg/L. Accordingly, As(III) will be highly mobile at an As concentration above 100 μg/L, but strongly retarded at a lower As concentration. Poor fits to the isotherm data were obtained using the state-of-the-art surface complexation model (CD-MUSIC) for goethite and, for comparison, the Dzombak and Morel (1990) generalized two-layer model for ferrihydrite. Both models strongly underestimated the sorption at a low As concentration. Apparently, either iron oxides like goethite do not control the As mobility, or the surface sites controlling As adsorption are not characterized in the models.

The mobility of As in the reduced aquifer was further assessed in a small-scale pumping experiment on the bank of a channel in the Dan Phuong field site. The groundwater at the test site had an As concentration of 250 µg/L, whereas the channel water had a negligible As concentration. The infiltrated channel water was enriched in As at a concentration of ~150 µg/L. A transport model indicated that As enrichment occurred during the passage through the fine-grained channel bed sediments, as opposed to a release from the sandy aquifer sediments, and confirmed the conclusion made from the isotherm, that transport of As(III) within the aquifer at concentrations above 100 µg/L showed a near-conservative behaviour. The CD-MUSIC model for goethite and and the two layer model for ferrihydrite were applied to assess the effect on the As mobility by competitive sorption during the pumping experiment. However, the models did not fit the data. These observations have important implications for our ability to predict the mobility of As in aquifer sediments.

In light of the severity of the problem with As in the drinking water, the difficulties in achieving a consensus on the controls of As release to the groundwater should lead to a focus on treatment methods for the abundant low-As surface water resources and As contaminated groundwater. Promotion of household sand filters, which can remove part of the As in the pumped groundwater and are already widely used in the Red River delta, should be an important part of the mitigation of the As problem. The possibility of As mitigation by bank infiltration of low-As river water was investigated as part of this thesis. The observed rapid release of As from river bed sediments, however, is a challenge for bank infiltration schemes, as further treatment to remove As from the infiltrated river water will be necessary. The removal efficiency by sand filtration increases with increasing Fe/As ratio in the raw water. Bank infiltrated river water may have a lower Fe/As ratio than groundwater, limiting the As removal efficiency by sand filtration. Based on the result presented in the thesis, bank infiltration, as a pre-treatment step in the utilization of river water, can only be recommended if the groundwater resource is subject to overexploitation. This is the case near Hanoi, but not currently in rural areas of the Red River delta.

# Resumé

Naturligt frigivet arsen (As) i grundvand brugt til drikkevand udgør en trussel for millioner af menneskers helbred i Sydøstasien. Det er estimeret, at 10 millioner mennesker, alene i den Røde Flod deltaet i Vietnam, er i risiko for at udvikle alvorlige og ultimativt dødelige sygdomme på grund af forgiftning med As i deres drikkevand.

Tidligere undersøgelser af UNICEF og det schweiziske EAWAG viser, at grundvand med en forhøjet koncentration af As forekommer i tydeligt afgrænsede geografiske områder i den Røde Flod deltaet. Som en del af nærværende PhD studie blev sammenhængen mellem geologien og forekomsten af As i grundvandet blevet undersøgt, på grundlag af vandprøver og geofysiske logs indsamlet langs et 50 km langt transekt over den sydlige og centrale del af deltaet. Den Kvartære lagfølge på op til 70 m i den sydvestlige del af transektet, udgøres her hovedsagligt af Holocænt mørkegråt, estuarint ler og fluvialt sand. I den nordøstlige del af transektet øges tykkelsen af den Kvartære lagfølge til 150 m og lagfølgen domineres her af grå-gulligt alluvialt sand og estuarint ler. Forhøjede koncentrationer af opløst $Fe^{2+}$, $HS^{-}$, $NH_4^{+}$ og $CH_4$, og fravær af $SO_4^{2-}$, blev observeret i de Holocæne sedimenter, sammenlignet med koncentrationerne i de Pleistocæne sedimenter, der desuden indeholdt opløst $SO_4^{2-}$. De Holocæne sedimenter er således tilsyneladende stærkt reducerende, i sammenligning med de Pleistocæne sedimenter. Fordelingen af opløst As i transektet forekommer at være styret af redox-miljøet. Høje koncentrationer af opløst As, op til 900 µg/L, blev observeret i den sydvestlige del af transektet, hvorimod koncentrationer af As under 25 µg/L blev observeret i den nordøstlige del af transektet. Den observerede fordeling af opløst As i transektet kunne relateres til den palæo-hydrogeologiske udvikling i den Røde Flod deltaet. Istiden i Sen-Pleistocæn bevirkede et lavt eustatisk havniveau, og den Røde Flod eroderede på det tidspunkt en dal langs den sydlige kant af deltaet. De til dalen tilstødende Pleistocæne sedimenter blev oxideret grundet et dybt beliggende grundvandsspejl, samt gennemstrømning af oxiderende grundvand på grund af de daværende øgede hydrauliske trykgradienter. Den efterfølgende Holocæne havniveaustigning bevirkede en hurtig sedimentation i dalen. Undersøgelsestransektets sydvestlige ende skærer de Holocæne sedimenter, som fyldte den begravede dal, og i hvilke der forekommer grundvand med en høj koncentration af As. Transektets nordøstlige del skærer de oxiderede Pleistocæne

sedimenter, der generelt indeholder grundvand med en lav koncentrations af As. Tilstedeværelsen af jernoxider, samt en nedsat reaktivitet af det tilbageværende organiske stof, forebygger muligvis en mobilisering af As. Det er desuden muligt, at der blev As blev skyllet ud med det gennemstrømmende grundvand under Sen-Pleistocæn.

De hydrologiske og geokemiske processer der er styrende for forekomsten af As i grundvandet i den Holocæne aquifer blev undersøgt på en feltlokalitet beliggende på en sand barre nær landsbyen Dan Phuong, 30 km opstrøms den Røde Flod fra Hanoi. Mössbauer-analyse af sedimenter indsamlet fra flodbunden og den tilstødende aquifer påviste et indhold af mikrokrystallinsk goethit samt mindre mængder hæmatit. En parallel frigivelse af As og Fe(II) blev observeret ved mikrobiel reduktion af Fe(III) med naturligt organisk stof eller acetat i inkubationer, samt ved abiotisk reduktion af Fe(III) med askorbinsyre i kinetiske ekstraktioner. Rækkefølgen ved hvilken As og Fe(II) frigives i inkubationerne, samt oxidationstrinnet for det frigivne As, kunne relateres til det relative redoxpotentiale mellem redoxparrene $Fe(OH)_3/Fe^{2+}$ og As(V)/As(III). Ifølge den termodynamiske analyse er As indbygget i jernoxiderne som As(V), der reduceres til As(III) efterhånden som As(V) blottes på overfladen under den reduktive opløsning af jernoxiderne. Resultaterne er i overensstemmelse med det nuværende paradigme for årsagen til den geografisk udbredte forekomst af As i grundvandet i Sydøstasien. Dette paradigme forskriver, at As er associeret til jernoxider og frigives herfra ved den reduktive opløsning af jernoxiderne samt ved reduktion af As(V), i begge tilfælde som følge af mikrobielt styrede processer der drives af oxidation af organisk kulstof.

Der blev på feltlokaliteten ved Dan Phuong observeret en frigivelse af As fra flodbundssedimenterne, og en efterfølgende transport af den opløste As med den naturlige grundvandsstrømningen til den underliggende reducerede aquifer, hvilket indikerer en betydelig mobilitet af opløst As i den reducerede aquifer. Laboratorieforsøg med sediment fra den reducerede aquifer viste at adsorptionen af As(III) til dette sediment følger en stærkt ikke-lineær isoterm for koncentrationer af opløst As under 100 μg/L. Ved As koncentrationer derover nærmer sorptionskapaciteten sig gradvist 1 μg/g sediment, ved en opløst koncentration af As på 250 μg/L. Isotermens form indikerer en høj mobilitet af opløst As(III) ved koncentrationer over 100 μg/L, mens en kraftig retardation af As fronten vil finde sted ved lavere opløste koncentrationer af As. Det blev efterfølgende forsøgt at opstille en computermodel for den målte isotherm. To teoretiske overfladekomplekseringsmodeller blev bragt i anvendelse: CD-MUSIC modellen for goethit (state-of-the-art) samt, til sammenligning, den generaliserede to-lagsmodel for ferrihydrit. Begge modeller underestimerede adsorptionen af As ved lave koncentrationer af opløste As. Dette indikerer at jernoxider, som goethit, enten ikke er styrende for mobiliteten af As i den reducerede aquifer, eller at de overfladepladser som kontrollerer sorptionen af As til jernoxiderne ikke er karakteriserede i modellerne.

En yderligere undersøgelse af mobiliteten af opløst As i den reducerede aquifer blev foretaget ved gennemførelsen af et små-skala pumpeforsøg på bredden af en kanal der gennemløber feltlokaliteten i Dan Phuong. Grundvandet på testlokaliteten havde en koncentration af opløst As på 250 µg/L, mens koncentrationen af As i vandet i kanalen var under detektionsgrænsen på 1 µg/L. Det ved pumpningen infiltrerede vand fra kanalen viste sig imidlertid at være beriget i As til en koncentration på ~150 µg/L. Det blev ved opstilling af en transportmodel for grundvandsstrømningen indikeret, at berigelsen med As foregik under vandets passage gennem flodbundssedimentet, snarere end fra aquiferens sediment. Resultaterne fra transportmodellen understøttede desuden konklusionen fra den målte isoterm, i at transporten af opløst As(III) forekommer at være tilnærmelsesvis konservativ ved koncentrationer over 100 µg/L. Til tolkningen af feltforsøget blev CD-MUSIC modellen for goethit og Dzombak and Morel (1990)'s to-lagsmodel for ferrihydrit benyttet til at vurdere effekten fra konkurrence med andre ioner om sorptionspladserne på mobiliteten af As(III). Ingen af de to modeller viste sig imidlertid i stand til at reproducere de observerede feltdata. Disse observationer har stor betydning for vores evne til at forudsige mobiliteten af opløst As i reducerede aquifersedimenter.

Den manglende konsensus om de styrende processer for frigivelsen af As til grundvandet må, i lyset af alvorligheden af problemet med As i drikkevand, føre til en øget fokus på metoder til behandling af såvel grundvand med et forhøjet indhold af As samt af de allestedstilgængelige overfladevandsressourcer, der generelt har et meget lavt indhold af As. En metode til herved at afhjælpe problemet med As, bør være at fremme udbredelsen af husholdningsbaserede sandfiltre. Passage af det oppumpede grundvand gennem et sandfilter kan fjerne betydelige mængder af den opløste As, og anvendelsen af disse selvbyggede sandfiltre er allerede udbredt i den Røde Flod deltaet. I nærværende PhD studie blev muligheden for langs flodbredden at benytte kunstigt infiltreret flodvand undersøgt. Den hurtige frigivelse af As fra flodbundssedimentet til det infiltrerende flodvand komplicerer imidlertid anvendelsen af denne metode, og det vil sandsynligvis være nødvendig at efterbehandle det oppumpede råvand. Ved en efterbehandling ved sandfiltrering, vil fjernelseseffektiviteten for As øges som funktion af et højere Fe/As-forhold i råvandet. Hvis det infiltreret flodvand har et lavere Fe/As-forhold end grundvand, kan efterbehandlingen derfor vanskeliggøres betydeligt. Baseret på resultaterne fra dette PhD studie, kan kunstig infiltration langs flodbredden kun anbefales hvor en overudnyttelse af grundvandsressourcen forekommer. Dette er tilfældet omkring Hanoi, men ikke i øjeblikket i landområderne i den Røde Flod deltaet.

# Preface

This PhD thesis deals with the presence of groundwater arsenic, which poses a real threat to the health of millions of people all over the world. The chapters 1 to 5 presents the results of the PhD research in a broader scientific context. Based on the findings of chapters 1 to 5, chapter 6 concludes by giving specific recommendations for the Vietnamese National Arsenic Action Plain to strategic mitigation measures for the groundwater As problem in the Red River flood plain in Vietnam. The PhD research results are formulated in the following five journal papers, included in appendix I to V:

**I** Postma D., Larsen F., Nguyen T. M. H., Mai T. D., Pham H. V., Pham Q. N. and Jessen S. (2007) Arsenic in groundwater of the Red River floodplain, Vietnam: Controlling geochemical processes and reactive transport modeling. *Geochim. Cosmochim. Acta* **71**, 5054–5071.

**II** Larsen F., Pham Q. N., Dang D. N., Postma D., Jessen S., Pham H. V., Nguyen B. T., Duc T. H., Luu T. T., Nguyen H., Chambon J., Nguyen V. H., Hoang D. H., Nguyen T. M. H., Mai T. D. and Refsgaard J. C. (2008) Controlling geological and hydrogeological processes in an arsenic contaminated aquifer on the Red River flood plain, Vietnam. *Appl. Geochem.* **23**, 3099–3115.

**III** Jessen S., Larsen F., Postma D., Pham H. V., Nguyen T. H., Pham Q. N., Dang D. N., Mai T. D., Nguyen T. M. H., Duc T. H., Luu T. T., Hoang D. H. and Jakobsen R. (2008) Palaeo-hydrogeological control on groundwater As levels in the Red River delta, Vietnam. *Appl. Geochem.* **23**, 3116–3126.

**IV** Postma D., Jessen S., Nguyen T. M. H., Mai T. D., Koch C. B., Pham H. V., Pham Q. N. and Larsen F. Mobilization of arsenic and iron from Red River floodplain sediments, Vietnam. Submitted to *Geochim. Cosmochim. Acta.*

**V** Jessen S., Postma D., Larsen F., Pham Q. N., Le Q. H., Tran V. L., Pham H. V. and Jakobsen R. The mobility of arsenic in a Red River floodplain aquifer: Results of a forced gradient experiment and surface complexation modelling. Manuscript.

The papers are not included in this www-version but may be obtained from the library at DTU Environment, Miljoevej, Building 113, Technical University of Denmark, DK-2800 Kgs. Lyngby (library@env.dtu.dk).

The research was carried out at DTU Environment between December 2005 and September 2009 and supervised by Dieke Postma, Flemming Larsen (both at GEUS), Rasmus Jakobsen (DTU Environment) and Pham Hung Viet (CETASD,

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Many thanks also to my fellow PhD students at DTU for the several years of good comradeship, Friday beers & cakes. Also thanks to the people at GEUS for providing a pleasant atmosphere everyday, and during Friday morning breakfasts and the occasional afternoon cake feasts.

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Lyngby, September 2009 Søren Jessen

# Table of contents

# 1 Introduction: The ‘arsenic problem’

Arsenic (As) in groundwater used for drinking water is slowly poisoning tens of millions of people all over the world. The extent of this disaster was not internationally recognized until the mid-1990s (Das et al., 1994; Dhar et al., 1997). Few years later more than every second well and borehole in Bangladesh were found to contain As above the 10 μg/L WHO guideline value (Chowdhury et al., 2000; BGS and DPHE, 2001). The ‘arsenic problem’ has become synonymous with the widespread groundwater As contamination in the densely populated South East Asian deltas, being the most severely As affected region worldwide.

Exposure to As causes *arsenicosis*, chronic arsenic poisoning. An early symptom of arsenicosis is hyperpigmentation which may develop after only a few years of exposure (Sampson et al., 2008). Longer-term As exposure causes skin cancer, acute myocardial infarction and several forms of internal cancer, such as cancers of the lung, bladder and kidney (Hopenhayn, 2006; Yuan et al., 2007). Yuan et al. (2007) studied the effects of arsenic exposure on the population of half-a-million in a Chilean region. Here, people were exposed to drinking water As concentrations of ~850 μg/L from 1958 to 1970. When the increased mortality from acute myocardial infarction, lung and bladder cancer peaked in the 1990s, an alarming 11% of all male deaths and 4% of all female deaths were due to the arsenic exposure 20 to 30 years earlier (Yuan et al., 2007).

Following recommendations from western aid programmes, the rural population in the Red River delta switched their drinking water supply during the mid-1990s, from surface water, often contaminated by pathogenic bacteria, to groundwater free of pathogens (Berg et al., 2001). Unfortunately, the groundwater was found to be contaminated by naturally occurring As (Berg et al., 2001; Giger et al., 2003). Groundwater and drinking water concentrations of As above the WHO guideline limit are now posing a risk for an estimated 10 million people in the delta (Berg et al., 2007). Individuals suffering from arsenicosis have been identified as early as in 2004 (Berg et al., 2006; Nguyen et al., 2009) and the need for immediate As mitigation actions has been stressed (Charlet and Polya, 2006; Berg et al., 2007).

The PhD research presented in this thesis was conducted in the Red River delta. Detailed field studies of the hydrogeological and geochemical processes controlling the release and mobility of arsenic were conducted at a field site located near Dan Phuong village, on a point bar 30 km upstream the Red River from Hanoi. Here, more than 200 observation boreholes have been installed since 2004. Parallel to these studies, the regional distribution of groundwater As, and its relation to the palaeo-hydrogeology was assessed by sampling monitoring wells along a 50 km transect crossing the Red River delta.

Drinking water is considered a major exposure route for As to the people living in groundwater As affected areas in South East Asia (Meharg, 2004; Mondal and Polya, 2008; Rahman et al., 2008). However, rice and other crops accumulate As, if groundwater contaminated by As is used for irrigation (Meharg and Rahman, 2003; Dittmar et al., 2007; Roberts et al., 2007). Therefore rice has become recognized as a second major human exposure route for As in regions like the Bengal delta, where groundwater is extensively used for irrigation (Meharg, 2004; Mondal and Polya, 2008; Roychowdhury, 2008; Brammer, 2009; Brammer and Ravenscroft, 2009).

# 2 Source and mobilization of As

The Red River delta, and other South East Asian deltas, ultimately derive their sediments from the Himalayas (Datta and Subramanian, 1997; Stummeyer et al., 2002; Stanger, 2005; Charlet and Polya, 2006; Guillot and Charlet; 2007). Arsenic is sorbed to neo-formed iron oxides in the sediment, and hence co-deposited on the delta plain in channels, point bars and overbank deposits which eventually form new aquifers (Nickson et al., 1998; Stummeyer et al., 2002; Raymahashay and Khare, 2003). Elevated groundwater concentrations of As occur when the As is released from the sediments. Hence the source of the As contaminating the groundwater in large areas of the South East Asian deltas is natural in origin.

## 2.1 Arsenic release from channel bed sediments

The mechanisms of the release of As from newly deposited sediments was investigated as part of this thesis (Jessen et al., manuscript). A river bed sediment was incubated with river water, to simulate the above described sequence of sediment deposition followed by burial into an aquifer. Both As and $Fe^{2+}$ was concomitantly released from a muddy Red River bed sediment within a few days (Fig. 1). Addition of acetate as an energy source available to microbes, lead to an increased release of $Fe^{2+}$ and As, suggesting that the release of As is linked to microbial reductive dissolution of As-bearing Fe(III) oxides.

As shown in Fig. 1, the As released in the incubation was almost entirely in the

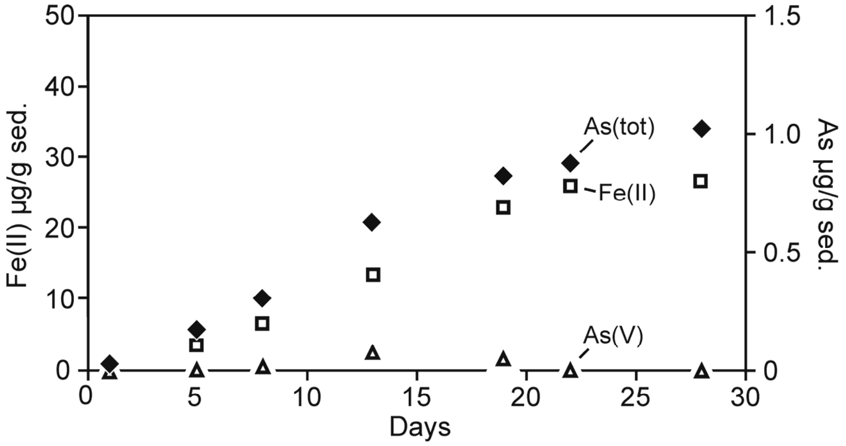

**Fig. 1.** Release of As and Fe from an incubated muddy Red River bed riverbed sediment.

reduced form as As(III), which is also the dominant As redox species in the groundwater of reduced aquifers. However, when the Fe(III) in the mud was abiotically reduced by ascorbic acid, a significant part of the As was released as As(V) (Postma et al., submitted), indicating that microbial As(V) reduction to more mobile As(III) contributed to the As mobilization, as previously reported by others (Islam et al., 2004, 2005). Heimann et al. (2007) demonstrated that As(V)-reducing bacteria are present in Red River delta sediments.

The sequence by which As and Fe is released from sediments as the conditions in the groundwater becomes more reducing is related to the redox potential of the $Fe(OH)_3/Fe^{2+}$ couple relative to that of the As(V)/As(III) couple (Islam et al., 2004; Burnol et al., 2007; Postma et al., submitted). Fig. 2 shows a pe-pH diagram for As, on which the $Fe(OH)_3/Fe^{2+}$ redox couple stability lines for ferrihydrite, goethite and hematite are superimposed. For a typical circum-neutral groundwater pH (6 to 8), the redox transformation of As(V) to As(III) precedes the reduction of Fe(III) in goethite and hematite to $Fe^{2+}$, and is more or less concomitant with the reduction of ferrihydrite-Fe(III) (Fig. 2).

In our sediments, goethite and hematite, but not ferrihydrite, were identified by Mössbauer spectroscopy. Therefore, the reduction of As(V) adsorbed or surface

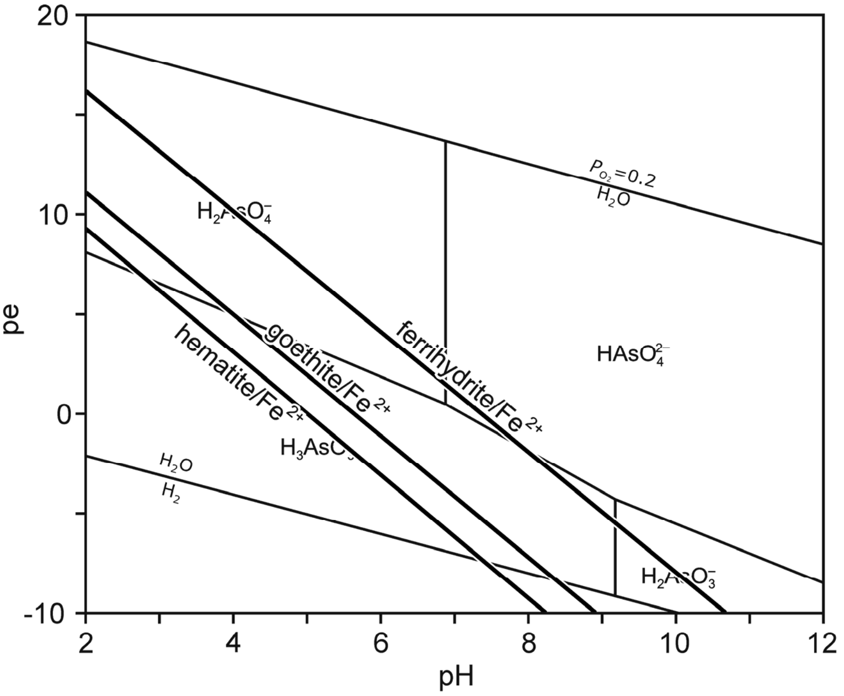

**Fig. 2.** pe-pH redox diagram for the As(V)/As(III) and $Fe(OH)_3/Fe^{2+}$ redox couples.

exposed on the iron oxides should precede the reduction of surface-Fe(III). The concurrent release of As(III) and $Fe^{2+}$ in the incubations (Fig. 1) hence corresponds to a situation where the As is incorporated into the iron oxides, at least partly as As(V), and reduced to As(III) when As(V) gradually becomes exposed during the reduction of the iron oxide. The sequence of As and Fe release from aquifer sediments often corresponds to a relatively stable iron oxide assemblage (van Geen et al., 2004; Gault et al., 2005; Anawar et al., 2006; Postma et al., submitted). In contrast, $Fe^{2+}$ release preceded As(III) release from aquifer sediments incubated by Islam et al. (2004), suggesting the presence of ferrihydrite in their sediment (Burnol et al., 2007). Redox-speciation of As in reduced sediment from West Bengal and Cambodia has shown the presence of As(V) (Rowland et al., 2005). Pedersen et al. (2006) showed that As(V) may be incorporated into goethite, but remains associated to the surface of ferrihydrite.

The above experimental observations are consistent with the current paradigm for the widespread As contamination in South East Asia which prescribes that As is associated with iron oxides (or mixed valence iron minerals such as magnetite), and released by microbially mediated reductive dissolution of the As-containing iron oxides (Nickson et al., 2000; Berg et al., 2001, 2008; McArthur et al., 2001, 2004; Harvey et al., 2002; Ahmed et al., 2004; Islam et al., 2004; Horneman et al., 2004; Swartz et al., 2004; Acharyya and Shah, 2007; Postma et al., 2007) and As(V) reduction (Dowling et al., 2002; Islam et al., 2005; Heimann et al., 2007) and both of these reductive processes are driven by the oxidation of organic carbon.

## 2.2 Hydrogeological control on As in groundwater

Recent studies suggest an important control by the local geochemistry and hydrology on the concentration of As in the groundwater. The often patchy distribution of groundwater As concentrations has been related to the near-surface lithology, causing locally elevated recharge rates in areas with a relatively high surface cover permeability and thereby preventing As from accumulating in the groundwater (van Geen et al., 2006; Stute et al., 2007; Aziz et al., 2008; Larsen et al., 2008; Hoque et al., 2009). Stute et al. (2007) proposed that new tube wells could be installed in the shallow aquifer underneath such high-recharge areas.

A more complex and intimate relationship between hydrology and geochemistry, however, was demonstrated for a natural setting in the Mekong delta by Polizzotto et al. (2008). At their field site, infiltration through young sediments deposited in wetlands or ponds, from which As was rapidly released, mobilized As to the down-gradient aquifers otherwise low in As. In the Red River delta, also Berg et al. (2008) observed a high As concentration in groundwater partially derived from ponds as indicated by $^{18}O$ and $^{2}H$ analysis, but only for locations between the dike and the Red River where fresh sediments were occasionally supplied by flooding. A low As concentration was observed in surface water-sourced groundwater behind the dike away from the river. Apparently, in the study by Berg et al. (2008) the geochemistry, particularly the organic matter abundance and reactivity, overprints the hydrological regime, in relation to groundwater As levels (c.f., Papacosta et al., 2008; Quicksall et al., 2008).

The location and mobility of the carbon source driving the As release processes, as well as the potential influence of human activities, remain contentious (Harvey et al., 2002; Klump et al., 2006; Meharg et al., 2006; Polizzotto et al., 2006, 2008). The results in Fig. 1 illustrate that the organic carbon co-deposited with the Red River bed sediment is reactive and abundant enough to cause a significant and surface-near As release. This supports the results of Polizzotto et al. (2008) and others (Acharyya and Shah, 2007; Berg et al., 2008). In Bangladesh, the vertical distribution of groundwater As in the Holocene aquifer generally shows a ‘bell-shape’, typical for vertically dispersed lateral transport of point-sourced contaminant plumes (BGS and DPHE, 2001; Harvey et al., 2005). Harvey et al. (2002) showed for a Bangladesh aquifer that dissolved inorganic carbon was significantly younger than both the dissolved and detrital organic carbon at the As-peak depth, dismissing the role of detrital organic matter degradation in mobilizing As. They proposed that irrigation pumping could explain the mobilization of As at well depth, and later provided $^{3}H$ and $^{18}O$ isotope data to support this (Harvey et al., 2005). Nevertheless, the release of As within the aquifer due to reductive dissolution of host minerals by detrital organic carbon have been reported by others for all the major South East Asian deltas (Berg et al., 2001, 2007, 2008; McArthur et al., 2001; Ravenscroft et al., 2001; Stüben et al., 2003; Meghar et al., 2006; Postma et al., 2007; Stute et al., 2007).

On our field site in Dan Phuong, 30 km upstream the Red River from Hanoi, As becomes mobilized both surficially in channel bed sediment (Larsen et al., 2008) and within the reducing aquifer sediments (Postma et al., 2007; Postma et al., submitted). At the Dan Phuong field site, the variation of the stable isotopic composition of water in the Red River and in the local precipitation provides a signature by which surface water recharge can be distinguished from precipitation recharge (Larsen et al., 2008). Infiltrated surface water had an As concentration of 75 to 300 µg/L, suggesting, since the As concentration in the surface water is negligible, a release of As within the channel bed (Larsen et al., 2008). At another location in the Dan Phuong field site, precipitation recharges the Holocene aquifer through fractures in the clay cover. Here the concentration of As gradually increases from below the limit of detection at the groundwater table, to more than 500 µg/L at 10 m depth below the water table. $^3H/^3He$-dating indicated a downward velocity component of the groundwater flow of 0.5 m/year, yielding an As release rate of roughly 20 µg/L/year, in good agreement with previously published results from Bangladesh (Stute et al., 2007).

The studied Holocene aquifer in Dan Phuong is very young, ~400 years (Larsen et al., 2008), compared to the 2,000 to 4,000 years old Bangladeshi aquifer studied by Harvey et al. (2002) and the 6,000 years old aquifer studied by Polizzotto et al. (2008). Probably the reactivity of the organic carbon in our young aquifer is higher than that of these older aquifers, facilitating the As release at depth in Dan Phuong. Indeed, As concentrations increased upon the injection of organic carbon to the Bangladeshi aquifer (Harvey et al., 2002), indicating that mobilization of As from the aquifer sediment is limited by the supply of reactive organic carbon from the surface.

Hence, in the South East Asian deltas high levels of As mobilization under natural conditions has been observed, but alterations in the hydraulic regime and/or the supply of carbon or As source material will affect the groundwater As concentrations (Polizzotto et al., 2008; Postma et al., 2007; Larsen et al., 2008; Berg et al., 2008). Where sedimentation has not ceased due to dike construction and flow regulations of the major rivers, the deposition of As-loaded sediments carried by the rivers results in a continuous flux of As to the delta aquifers (Polizzotto et al., 2008). Alternatively, where flooding control has caused sediment deposition to cease, mass balance estimates indicate that decades to millennial timescales are required before aquifers are flushed for their sedimentary As content (Postma et al., 2007; Larsen et al., 2008; van Geen et al., 2008). Pumping will affect such flushing because it perturbs the hydraulic regime (Harvey et al., 2002). In the Red River delta, surface water is still the dominant source for irrigation (WRCS, 2000; Berg et al., 2008). In the Bengal delta, large amounts of groundwater is pumped for irrigation, possibly affecting the groundwater As concentration (Harvey et al., 2005; Shamsudduha et al., 2009).

## 2.3 Mobility of As in reduced aquifer sediments

Once As has been released from the sediment, its transport through the aquifer with the groundwater flow may be controlled by sorption to the aquifer sediments and, possibly, by co-precipitation with secondary phases such as iron sulphides or siderite. An adsorption isotherm for As to the reduced aquifer sediment from the Dan Phuong field site (Fig. 3) was determined as part of this thesis (Jessen et al., manuscript). The sorption of As(III) to the reduced sediment conforms to a strongly non-linear adsorption isotherm below an As concentration of ca. 100 µg/L. At a higher dissolved As concentration (>100 µg/L), the sorption increases to ca. 1 µg As per g sediment for a dissolved As concentration of ca. 250 µg/L. This implies that As(III) will be highly mobile at an As concentration above 100 µg/L, but strongly retarded at a lower As concentration (Jessen et al., manuscript).

The mobility of dissolved As was assessed *in situ* by conducting a small-scale

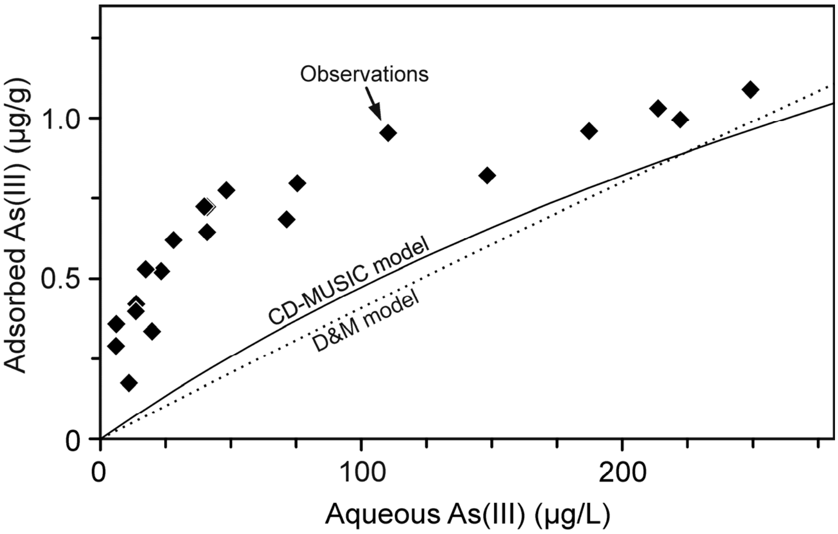

**Fig. 3.** As(III) adsorption isotherm to reduced Holocene aquifer sediment. Model lines for the CD-MUSIC model for goethite and the Dzombak and Morel (1990) model for ferrihydrite are indicated.

field pumping experiment in Dan Phuong. During the pumping, the concentration of groundwater As decreased from 250 to 150 µg/L as water with a lower concentration of As replaced the unperturbed groundwater. Dissolved As showed no retardation relative to the major solutes in the groundwater (Jessen et al., manuscript), hence supporting the conclusion made from the isotherm data (Fig. 3), that at a groundwater As concentration above 100 µg/L, dissolved As is highly mobile in the reduced aquifer sediments. A similar conclusion was made by Harvey et al. (2002).

We attempted to model the adsorption of As(III) to the reduced Holocene aquifer sediment (Fig. 3) using surface complexation models (Jessen et al., manuscript). While our investigations have shown the presence of goethite (and subordinary amounts of hematite) in the reduced sediment (Postma et al., submitted), the state-of-the-art surface complexation model (CD-MUSIC) for goethite did not reproduce our As(III) adsorption data (Fig. 3). Also the generalized two-layer model for ferrihydrite by Dzombak and Morel (1990) did not fit our data. This indicates that iron oxides like goethite, or minerals with similar sorption affinity for As(III), such as magnetite (Dixit and Hering, 2003; Swatz et al., 2004) either do not control the As mobility, or the surface sites controlling As adsorption at natural conditions are not characterized in the models (Pontieu et al., 2006). This observation has important implications for our ability to predict As mobility and flushing of As from aquifer sediments.

## 2.4 Other processes controlling As release and cycling

As noted early by Chowdhury et al. (1999), the association of As to iron oxides appears to be just one of several controls on As levels in the groundwater. Polizzotto et al. (2006), using X-ray absorption spectroscopy with a detection limit of 5% of total iron, did not identify iron oxides throughout the Holocene aquifer at a Bangladesh study site. However, surface complexation modelling indicated that less than 5% of the total iron, if present as magnetite or goethite, would yield the observed distribution of As(III) between the solid and solution phase (Harvey et al., 2002; Swartz et al., 2004). Others have detected ferrihydrite, goethite and hematite in As-affected South East Asian aquifer sediments (Akai et al., 2004; Rowland et al., 2008; Postma et al., submitted).

Weathering of As-containing micas has been proposed as a source of As (Seddique et al., 2008, 2009; Dowling et al., 2002), though disputed by others

(Anawar and Mihaljevič, 2009), and groundwater As levels may be controlled by adsorption to micas (Chakraborty et al., 2007), clay minerals (Lin and Puls, 2000; Goldberg, 2002) and carbonate minerals (Sø et al., 2008) which, being abundant in the aquifer sediments, may have a substantial sorption capacity. The displacement of As by competitive solutes, especially the strongly adsorbed phosphate, but also the less strongly adsorbed but abundant carbonate and silicate ions, has been observed in synthetic systems (Swedlund and Webster, 1999; Dixit and Hering, 2003; Radu et al., 2005) and predicted by theoretical models for aquifers (Appelo et al., 2002; Stachowicz et al., 2007). Fertilizer-phosphate, and carbonate as a reaction product of organic matter degradation, have therefore been proposed to cause As mobilization in the aquifers (Acharyya et al., 1999; Appelo et al., 2002, Anawar et al., 2003, 2004; Stachowicz et al., 2007). The co-occurrence of $Fe^{2+}$ with As(III) in reducing waters may work oppositely by increasing the adsoption of As(III) to goethite via the formation of a ternary Fe(II)-As(III) surface complex (Hiemstra and van Riemsdijk, 2007; Berg et al., 2008).

Oxidation of arsenical pyrite due to water table drawdown by pumping (Bagla and Kaiser, 1996; Das et al., 1996; Mandal et al., 1998; Chowdhury et al., 1999) was early dismissed as the main mechanism for the widespread As contamination (Nickson et al., 1998, 2000; McArthur et al., 2001; Ravenscroft et al., 2001), but Polizzotto et al. (2006) later suggested a refined model for a near-surface As mobilization via As-S-Fe redox cycling in the seasonally saturated-unsaturated (i.e., oxic-anoxic) zone and as evidence noted the presence of both detrital and authigenic pyrite in their sediment. The importance of this cycling, however, remains unclear. A significant release of sulphate during oxidizing cycles, for instance, has not been observed (Chowdhury et al., 1999), but this may be due to too low sampling resolution as the sulphate liberated may become trapped in sulphate minerals like $FeSO_4$ (Das et al., 1996) or iron sulphides in the sulphate reducing zone (Chowdhury et al., 1999). Sulfur cycling has more often been reported to scavenge As by iron sulphide precipitation (McArthur, 1999; McArthur et al., 2001; Stüben et al., 2003; Lowers et al., 2007; Jessen et al., 2008; Buschmann and Berg, 2009) and in As-S phases such as orpiment (Papacosta et al., 2008; Quicksall et al., 2008). Secondarily formed siderite and vivianite have also been proposed as scavengers of released As (Sengupta et al., 2004; Acharyya and Shah, 2007; Postma et al., 2007, Eiche et al., 2008; Thinnappan et al., 2008). Recently, microbial weathering of river-sourced Asrich apatite was proposed to be a significant internal source of As to the aquifers (Mailloux et al., 2009).

Hence, according to our current knowledge, several processes, both hydrogeological and geochemical, control the concentration of dissolved As in an aquifer. It is well established that iron oxides are an important initial host for As, which become released during reduction driven by organic carbon. However, the cycling of As in the soil and subsurface sediments appears to be controlled by a several processes, the importance of which remains unresolved. Charlet and Polya (2006) concluded, in relation to the urgency of the As problem, that the difficulties in achieving a consensus on the controls of As release to the groundwater should redirect the research focus to a safe utilization of the As-safe surface water resources.

# 3 Regional As distribution in the Red River delta

One of the aims of this thesis has been to evaluate in a hydrogeological context the regional distribution of groundwater As in the Red River delta. Two large As surveys have been carried out in the delta, prior to this study. The first one was lead by UNICEF from late 2003 to 2004 and the second by a co-operation between the Swiss EAWAG and the Centre for Environmental Technology and Sustainable Development (CETASD) at Hanoi University of Science (HUS). Unfortunately, to date no As distribution maps covering the Red River delta area based on these surveys have been made public. The UNICEF survey results were communicated in a proceedings paper (Badloe et al., 2004) on the Third Scientific Conference at HUS and in a UNICEF report (IET and VAST, 2004) presenting groundwater As distribution maps for some selected provinces. The EAWAG/CETASD results have not been published yet (Buschmann and Berg, 2009), but we were presented to the data at an early stage (Michael Berg, private communication).

The UNICEF survey tested 10,792 wells in five of the provinces in the Red River delta (Fig. 4A). The results are summarized in Fig. 4B. The three worst affected provinces, Ha Tay, Ha Nam and Nam Dinh, are situated along the Red River and here 30% to 50% of the tested wells contain more than 10 µg/L As. In Ha Nam

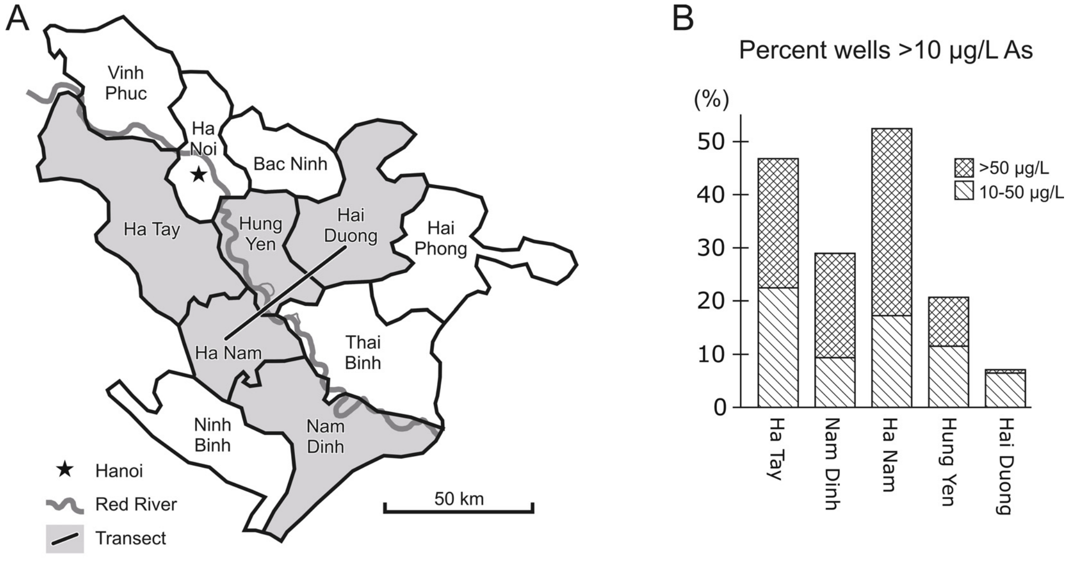

**Fig. 4.** (**A**) Provinces in the Red River delta covered by the UNICEF survey (shaded) and location of the present study transect. (**B**) Percent of tested wells exceeding 10 µg/L As. Data from Badloe et al. (2004).

province more than 30% of the tested wells extract water with an As concentration above 50 µg/L. Low groundwater As levels are found in the north-eastern part of the delta. In Hai Doung province, 6% of the tested wells contain between 10 and 50 µg/L and less than 1% contain more than 50 µg/L As. A very similar As distribution was found by the EAWAG survey (Michael Berg, private communication), which tested 461 randomly selected wells covering the delta area.

None of these investigations aimed directly at explaining the potential underlying geochemical or hydrogeological control on the groundwater As distribution. However, for the Red River delta a tentative ‘groundwater As risk map’ based on geological information, climate and land use (Berg et al., 2007) predicts a relatively similar As distribution trend to that observed by the regional surveys. In the Bengal delta, low-As groundwater can be pumped from older aquifers, which were oxidized during the Pleistocene (Ravenscroft et al., 2001, 2005) and this knowledge is now part of the As mitigation both in urban (Hug et al., 2008) and rural areas (von Brömsson et al., 2007). Based on the results from the EAWAG/CETASD survey, we therefore sampled national monitoring network wells along a transect line (Fig. 4 and 5) running from the high-As area into the low-As area, and established a geological model from a literature review and geophysical logging in the sampled wells (Jessen et al., 2008).

The Quaternary depositional environment in the Red River delta was controlled

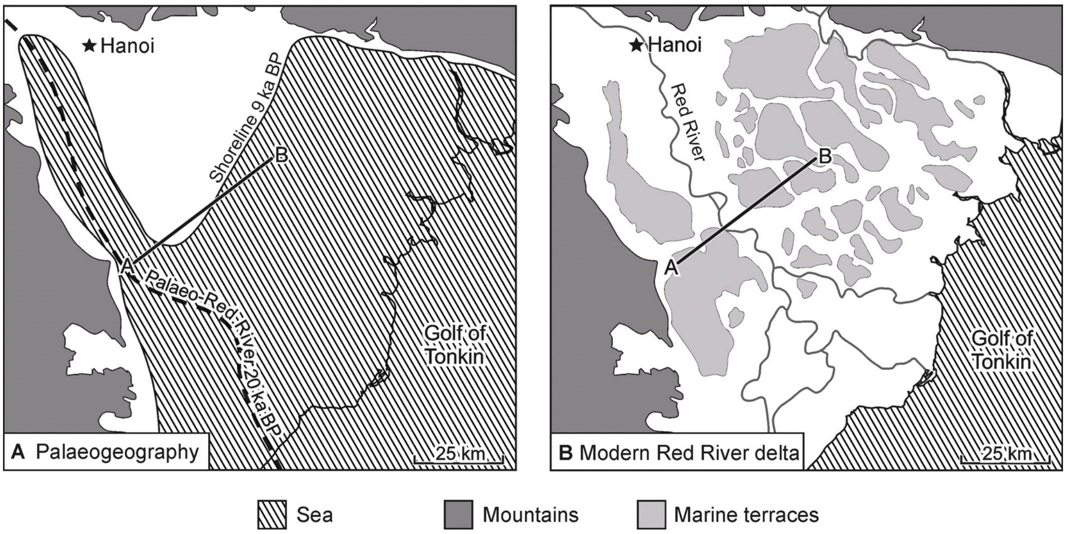

**Fig. 5.** The Red River delta: (**A**) palaeogeography and (**B**) modern delta.

in large part by changes in the eustatic sea level due to global temperature variations (e.g., Tanabe et al., 2006). The eustatic sea level decreased to 130 meter below the present sea level due to global cooling 20,000 years before present (BP), at the last glacial maximum, as sea water accumulated in terrestrial ice-sheets. The palaeo-Red River at that time eroded a valley into the Pleistocene sediments along the southern delta boundary (Fig. 5A). A transgression occurred at the termination of the glacial maximum. At 9,000 years BP the sea reached Hanoi via the incised valley, as shown in Fig. 5A. The maximum transgression occurred during the mid-Holocene, from 6,000 to 4,000 years BP, and an estuarine depositional environment then covered most of the delta plain. During the transgression the incised valley became rapidly filled with Holocene marine-estuarine silt and clay and deltaic sand (Tanabe et al., 2006). During the mid-Holocene transgression marine-estuarine sediments were deposited, present today as terraces in the Red River delta area, shown in Fig. 5B.

A hydrogeological cross section for the A-B transect (Fig. 4 and 5) is shown in Fig. 6. In the north-eastern half of the transect, Late Pleistocene sediments (ca. 30,000 to 50,000 years BP) comprise most of the Quaternary sequence. Here, the Pleistocene sediments are found at shallow depth, because basin tectonics have prevented the Red River from sweeping over the delta during the Late Pleistocene-Holocene (Tran et al., 2002). Earlier in Pleistocene, the centre of subsidence was located in the central-northern part of the delta (Tran et al., 2002), where, hence, the thick Pleistocene sediments are present (Fig. 6) (Mathers and Zalasiewicz, 1999). The Quaternary sequence in the south-western part of the transect is dominated by Holocene valley fills, deposited on top of a thin Pleistocene sequence.

Elevated concentrations of dissolved $Fe^{2+}$, $HS^-$, $NH_4^+$ and $CH_4$, and a low concentration of $SO_4^{2-}$, were observed in the Holocene valley fills, relative to the concentrations in the Pleistocene deposits, where, in addition, a higher concentration of $SO_4^{2-}$ was found (Jessen et al., 2008). Hence, the rapidly deposited Holocene valley fills appeared to be strongly reducing, compared to the Pleistocene deposits. The distribution of groundwater As was controlled by the redox environment. In the southern part of the transect, groundwater As concentrations up to 900 µg/L were observed, whereas lower As concentrations, <25 µg/L, were found in the northeast end of the transect. Also elevated As levels occur in the thin Pleistocene aquifer present underneath the Holocene incised valley fills, probably due to leaching of As and/or dissolved organic carbon from the Holocene sediments (Jessen et al., 2008). The study confirmed the As distribution found in the above mentioned two regional surveys (Jessen et al., 2008).

A low concentration of As is found in both the shallow Holocene (5–15 m) and deep Pleistocene (30–150 m) aquifer located to the north-east of the meander belt of the modern Red River. Both the shallow Holocene and the Pleistocene aquifer have less strongly reducing conditions relative to the As-affected aquifers in the incised valley.

Contrasting the typically grey-black colour of the Holocene sediments, the Pleistocene sediments north of the Red River are described as grey-yellow down to an elevation of -105 m. The oxidized colour of the Pleistocene sediments may be due to oxidation during the glacial maximum 20,000 years BP, when the eustatic sea level decreased to -130 m. A similar palaeo-hydrogeologically controlled oxidation of Pleistocene sediments in the Bengal delta have been reported (Ravenscroft et al., 2001, 2005). Iron oxides in the oxidized sediments may retard As and a decreased reactivity of the residual organic matter possibly prevents As (re)mobilization. In addition, As may have been flushed from the older aquifers by groundwater flow during the Pleistocene, as proposed for the Bengal delta by Ravenscroft et al. (2005). The shallow Holocene aquifer covering the oxidized Pleistocene aquifer was deposited at a low sedimentation rate (Lam and Boyd, 2003; Funabiki et al., 2007). This may have caused the burial of only more degraded organic matter, relative to the high deposition rate in the Holocene incised valley.

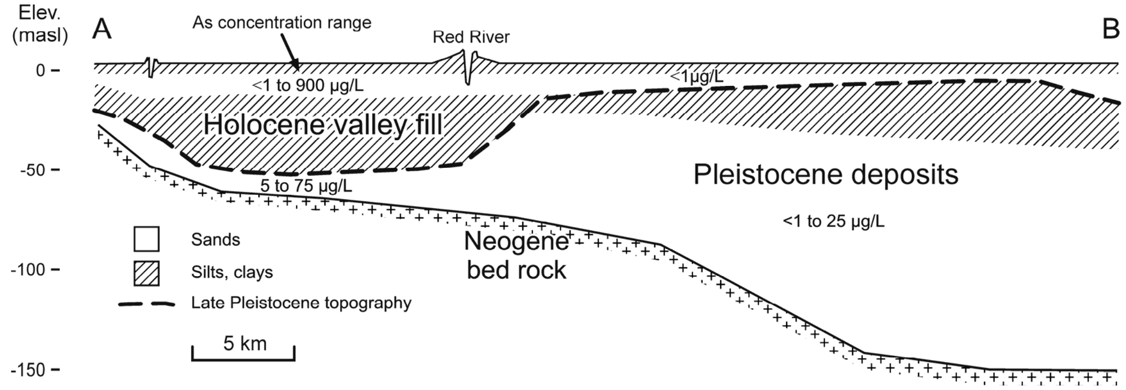

**Fig. 6.** Geological cross section of the sampled transect (A-B in Figs. 4 and 5). The dissolved As concentration range is indicated for the different parts of the transect.

In the Red River delta, the Pleistocene and Holocene aquifers are separated by Late Pleistocene and Early Holocene estuarine silt and clay units (Fig. 6). These units contain entrapped seawater which enters the aquifers by diffusion (Jessen et al., 2008). In addition, entrapped seawater derived from the mid-Holocene transgression is present in the marine-estuarine surface deposits covering a large part of the delta plain (Fig. 5B) (Jessen et al., 2008). This residual seawater locally increases the groundwater salinity in the Holocene aquifer. The reduction of seawater-derived sulphate and the following iron sulphide precipitation apparently impose an important sink for As (Jessen et al., 2008; Buschmann and Berg, 2009). However, the quality of the low-As groundwater is often limited by an elevated salinity (Jessen et al., 2008).

Accordingly, the distribution of groundwater As in the Red River delta is controlled by a combination of palaeo-hydrogeology and local basin tectonics during Late Pleistocene. An elevated groundwater As concentration is found in the Holocene aquifer, rapidly deposited during the sea level rise in an incised valley along the southern boundary of the Red River delta. Groundwater with a low As concentration is found in the central and northern part of the delta, but locally the quality is limited by an increased salinity.

# 4 Household sand filtration in the Red River delta

Many water treatment facilities worldwide apply aeration and sand filtration by which dissolved iron is removed from the raw water. This treatment also removes As which sorbs to the ferrihydrite formed by the oxidation of Fe(II) after the aeration (Carlson and Schwertmann, 1987; Jessen et al., 2005). The removal process hence utilizes the common co-occurrence of ferrous iron with As in the contaminated groundwater. The most important parameter for the efficiency of the removal process is therefore the ratio of dissolved iron-to-As in the raw water (McNeill and Edwards, 1997; Berg et al., 2006; Hug et al., 2008). The sorption affinity of As for ferrihydrite in natural waters depends on the As oxidation state (III or V), and As(III)-oxidation is therefore an important part of the treatment (Meng et al., 2002; Roberts et al., 2004; Jessen et al., 2005; Hug et al., 2008). In addition, solutes competing for sorption sites on the ferrihydrite surface, especially phosphate, may decrease the removal efficiency (Wilkie and Hering, 1996; Hering et al., 1997; Meng et al., 2000, 2002; Dixit and Hering, 2003; Berg et al., 2006; Hug et al., 2008).

Despite a similar geographical and geological setting, the As-affected South East Asian deltas have important differences in the groundwater Fe/As ratio and phosphate concentrations, as shown by Hug et al. (2008). This in turn affects the As removal efficiency of aeration and sand filtration. Generally, the groundwater in the Red River delta has both a high Fe/As molar ratio and a low concentration of phosphate relative to the Bengal and the Mekong deltas (Hug et al., 2008). Hence, generally, a higher As removal efficiency by sand filtration is expected in the Red River delta, relative to the other deltas.

Many private tube well owners in rural areas of the Red River delta have built aeration and sand filtration units to remove the iron and its metallic taste (IET and VAST, 2004; Berg et al. 2006; Hug et al., 2008). Interestingly, Berg et al. (2006) showed that As concentrations after treatment were below 50 µg/L in 90% of the studied sand filters, and 40% were below the 10 µg/L WHO guideline. One of the advantages of the treatment method is that no oxidants or other chemical additive is required. In addition, the knowledge of the sand filter construction and maintenance is shared among people. These results indicate a large potential of sand filtration for mitigation of the As problem in rural areas of the Red River delta, which are not supplied by centralized water treatment facilities.

Also concentrations of $Mn^{2+}$, which in the Red River delta are often above the 0.4 mg/L WHO guideline value (Agusa et al., 2006; Berg et al., 2006; Jessen et al., 2008) decreased in the sand filters indicating the formation of oxidized Mn-precipitates (Berg et al., 2006). Berg et al. (2006) proposed that a higher As removal efficiency than that predicted from the high proportion of As(III)/As(tot) in the raw water could be due to As(III) oxidation by the Mn. The oxidation of As(III) during the filter passage is likely significant. Complete As(III) oxidation by a surface reaction process was observed in a similar sand filtration unit in Denmark, albeit at a relatively low initial As(III) concentration (Jessen et al., 2005). Moreover, the filter medium in some of the units studied by Berg et al. (2006) contained 'black sand' coated by Mn oxides which would be able to rapidly oxidize increased amounts of As(III) (Driehaus et al., 1995; Scott and Morgan, 1995; Manning et al., 2002). However, the composition of the raw water (Fe/As and P), and not the filter medium, was reported to control the As removal efficiency (Berg et al., 2006), suggesting a comparable As(III) oxidation in all of the studied filter media. It should be noted that Mn removal was observed in all filters, suggesting that $Mn^{2+}$ release from the 'black sand' medium due to the addition of Mn-reducing Fe(II) with the raw water (Postma and Appelo, 2000) is not of concern. Arsenite may also become oxidized by Fe(IV) radicals formed during the Fe(II) oxidation by $O_2$ at neutral pH (Hug and Leupin, 2003; Leupin et al., 2005).

Installation of As removal plants (ARPs) to mitigate As in the Bengal delta were initiated in the late 1990s (Hossain et al., 2005, 2006). The installed ARPs each served 200 to 250 users on average (Hossain et al., 2006) and were technically more advanced relative to the Vietnamese household sand filters. However, in a review of the APRs performance, Hossain et al. (2005, 2006) concluded that one out of four ARPs was either not functioning or delivered water with an As concentration above 50 µg/L. In fact, shallow tube wells often contaminated with As continued to be the dominant source of drinking water for the population after an ARP has been installed (Hossain et al., 2005). The overall failure of the ARPs was ascribed in large part to a lack of community participation. In the Red River delta, the socially adopted, low-tech household-based sand filtration unit appears to be more successful (Berg et al., 2006).

A variety of small household water treatment (HWT) units have been developed and tested mainly in As-affected areas in the Bengal delta. Among these HWT units, the SONO filter has shown a large As removal efficiency and reliability at a minimum of maintenance (Hussam and Munir, 2007). Also the Kanchan As filter has shown promising results in Nepal (Ngai and Waliwijk, 2003, 2006), and is now being tested in Bangladesh and Cambodia. Both units work without addition of chemicals.

Used filter sand may contain high concentrations of As (Berg et al., 2006; Jessen et al., 2005) which can be released upon reduction of the As(V) or the iron oxide coatings (Förstner and Haase, 1998; Meng et al., 2001). Disposal of the used filter sand to (seasonally or future) reducing environments (e.g., ponds, rice paddy field) should therefore be avoided (Berg et al., 2006). As an alternative to disposal, the sand may be re-used in construction (Berg et al., 2006), as reported for As-laden water treatment sludge (Rouf and Hossain, 2003; Banerjee and Chakraborty, 2005; Jing et al., 2005).

# 5 The mitigation potential of bank infiltration

One of the main aims of this thesis was to investigate whether As-safe drinking water can be obtained by *bank infiltration*. Here, wells are placed sufficiently close to the river so that most of the abstracted water will be infiltrated river water (Stuyfzand, 1989). Bank infiltration from rivers is widely used in central Europe and is gaining use in the US, Brazil, South Korea and India (Stuyfzand, 1989; Hiemstra et al., 2003; Weiss, 2005; Schmidt et al., 2007; Kim and Kim, 2008; Ray, 2008). The passage of the infiltrated river water through the bed and aquifer sediments generally improves its quality and sufficiently removes pathogenic bacteria and viruses from the river water, even at short travel times (weeks to few months) and distances (tens of meters) (Stuyfzand, 1989; Weiss et al., 2005; Eckert et al., 2008; Hiemstra et al., 2003). Organic micropollutants in the river water, such as pesticides, pharmaceuticals, industrial chemicals and their metabolites, are removed by adsorption and biodegradation, albeit the degradation for some pollutants is most efficient under anaerobic relative to aerobic conditions, and visa versa for others (Schmidt et al., 2007).

The surface water and river water of the major rivers in the South East Asian deltas provide an abundant low-As water resource (BGS and DPHE, 2001; Agusa et al., 2006; Postma et al., 2007). Therefore several studies have proposed a return to surface water for drinking water, despite the obvious requirement for advanced treatment to remove pathogenic bacteria and other pollutants (Bagla and Kaiser, 1996; Hossain et al., 2005; Berg et al., 2008). In the Red River delta, the As concentrations in the treated water from the Hanoi water supply treatment plants is above the 10 µg/L WHO guideline value (Berg et al., 2001), and in addition Berg et al. (2008) listed a number of adverse effects on the raw water quality due to the excessive groundwater abstraction in the Hanoi area. Bank infiltration could become an important pre-treatment step (Ray, 2008) if Hanoi water supply switches from As contaminated groundwater to surface water as proposed by Berg et al. (2008).

The groundwater abstracted from the Pleistocene aquifer by the Hanoi water supply at present contains a considerable fraction of Red River water (Berg et al., 2008). The As in the abstracted water (15-430 µg/L, Berg et al., 2001) may be derived from the Pleistocene or overlying Holocene sediments (Berg et al., 2008), the river bed sediment, or be due to mixing with As containing groundwater, but the relative importance of these As sources is not yet quantified. The distance from the river to the well fields operated by the Hanoi water supply is between 5 and 10 km.

A new well field was recently established south of Hanoi in Nam Du, on the bank of the Red River resulting in travel distances of a few hundred meters (Norrman et al., 2008). The results from here may indicate a reduction in the concentration of As to about 75 µg/L in the pumped water. As in the case above, this As could originate from mixing with groundwater or a release from river bed or aquifer sediment.

Also in rural areas, the processes taking place during bank infiltration of river water potentially provide an alternative to the advanced surface water treatment while making use of the abundant low-As surface water resource. To tests this, we therefore conducted a small-scale pumping experiment on the bank of a channel in our Dan Phuong field site (Jessen et al., manuscript), hence imitating the conditions met during bank infiltration. The water in the channel has a low As concentration. However, the infiltrated channel water, forced to pass a set of observation wells by the pumping, was enriched in As at a concentration of ~150 µg/L. A transport model indicated that the As enrichment occurred during the passage through the young fine-grained channel bed sediments, as opposed to a release from the sandy Holocene aquifer sediments (Jessen et al., manuscript).

As described previously, an As release was observed both in incubations of river bed sediments (Fig. 1) (Postma et al., submitted) and in naturally infiltrated channel water at another field location in our study area in Dan Phuong (Larsen et al., 2008). Hence, our observations generally indicate that a significant release of As to the infiltrating surface water will occur in the channel bed. In addition, the As(III) adsorption isotherm to the reduced Holocene aquifer sediment, shown in Fig. 2, predicts that even in the case of an insignificant As release from the bed sediment, then the release of up to ~1.0 µg of labile As per g aquifer sediment may contaminate the abstracted water for several (possible tens to hundreds) pore volumes before an As concentration below the guideline value is achieved. Therefore, in rural areas, bank infiltrated water might require further treatment to remove As.

Noteworthy is, that the ratio of Fe/As ratio and concentration of phosphate in the bank infiltrated water may be less favourable for successful treatment for As, than that of non-river sourced groundwater. This was the case in our pumping experiment. For example, the percentage of As removed by sand filtration estimated according to Berg et al. (2006) from the concentration of dissolved Fe dropped from 78% in the original groundwater to 64% in the bank filtrate. Even at the lowered As concentration of the bank infiltrated water (from 250 to 150 µg/L) a higher final As concentration in the treated bank infiltrated water of 54 µg/L, relative to 50 µg/L in treated groundwater, is estimated. Hug et al. (2008) provided a simple relationship for assessing the As removal which infers a preferential removal of phosphate over As by sand filtration: $R_{\mathrm{As/Fe/P}} = (m_{\mathrm{Fe}} - 1.8 * m_{\mathrm{P}})/m_{\mathrm{As}}$ where $m$ denotes a concentration in moles of Fe, As and P, respectively. According to Hug et al. (2008) values of $R_{\mathrm{As/Fe/P}}$ above 54 are needed for efficient As removal. However, in our pumping experiment, $R_{\mathrm{As/Fe/P}}$ decreased from 61 in the unperturbed groundwater to just 30 in the infiltrated channel water. If these conclusions apply more generally, then bank infiltration appears to be preferable only if the groundwater resource becomes subject to excessive utilization, as is the case in Hanoi (Berg et al., 2008), but currently not in the rural areas of the Red River delta.

# 6 Concluding recommendations for As mitigation measures

## 6.1 The Vietnamese National Arsenic Action Plan

Despite more than a decade of intensive research aiming at mitigation of the As problem, the people in the Red River delta are still consuming As contaminated drinking water (Berg et al., 2001, 2008; Buschmann et al., 2007; Nguyen et al., 2009). In 2006, a National Arsenic Action Plan (NAAP) developed by the Ministry of Agricultural and Rural Development and UNICEF was approved by the Prime Minister of Vietnam. Current NAAP activities focus on information, education and communication and behavioural change communication, and these activities should continue to be a vital part of the overall As mitigation. Also As mitigation actions directed at providing alternative drinking water sources (e.g., sand filter optimization, implementation of HWT units, rain water harvesting, piped water) are ongoing, but appear to be geographically dispersed to a few selected districts or communes, compared to the information activities.

Importantly, the technology to lower As concentrations in drinking water exists and can be implemented immediately. Nevertheless, a diverse suite of mitigation actions is needed to cover the diversity of the As problem in the Red River delta. The management of the mitigation actions is the major challenge; the water resource is abundant.

## 6.2 Data requirements

Planners and decision makers should base the aiming of immediate mitigation actions on distribution maps for groundwater As and $R_{\mathrm{Fe/As/P}}$ (c.f., Hug et al., 2008). If these maps are not already available to the relevant people, they could probably be prepared from already existing data from regional surveys by UNICEF and EAWAG/CETASD. Arsenic mitigation actions should focus on areas with an elevated groundwater As concentration.

If the value of $R_{\mathrm{Fe/As/P}}$ shows a clear regional trend within areas elevated in As, a further division into high- and low-$R_{\mathrm{Fe/As/P}}$ areas can be made so that removal efficiencies by sand filtration and, potentially, estimates of the final As concentration in treated water can be mapped. However, it is possible that no trend in the distribution of the $R_{Fe/As/P}$ value within areas with elevated As will be apparent.

In addition, preliminary reports indicate a considerable regional variability in the source and treatment of drinking water (NIOEH, 2003; IET and VAST, 2004; Nguyen et al., 2009). In some areas households rely largely on rain water harvesting for drinking water, while sand filtration of groundwater is used in other areas (NIOEH, 2003), and this distribution should be investigated. Also, the distribution of people having access to drinking water from centralized water treatment plants, as opposed to people with a household-based drinking water supply, should be investigated and mapped.

Estimates of the number of people exposed to elevated As levels are crucial for the planning of mitigation actions. The present estimate of 10-11 million people at risk, i.e., the whole Red River delta population (Berg et al., 2001), is likely to be overestimated, as evident from the regional As distribution described above. Therefore the number of people in the Red River delta supplied with groundwater and drinking water with an As content exceeding national standard and WHO guidelines should be updated.

## 6.3 Centralized water treatment

Centralized water treatment plants (as in Hanoi) can be optimized to more efficiently remove As. For example, optimization by adjustment in the overall $R_{Fe/As/P}$ value can be overcome by mixing water from wells with a high $R_{Fe/As/P}$ value with water from wells with a low $R_{Fe/As/P}$ value. Oxidation of As(III) to As(V) will likely be significant during the passage of a sand filter (Jessen et al., 2005; Berg et al., 2006). Therefore Fe(II)-addition between serially connected sand filters has a large potential for improving the As removal efficiency. The performance and eventual optimization should be done individually for each treatment plant and this is as such a management challenge. People in areas covered by a centralized water treatment facility, but still using a private tube well, should be made aware of the possible As contamination and the benefits from shifting to the centralized supply.

Bank infiltration, as already initiated in Nam Du (Norrman et al., 2008), should be promoted where the groundwater resource is subject to excessive utilization. This is the case in Hanoi (Berg et al., 2008) and possibly in other cities along the

Red River. Close monitoring of the current bank infiltration along the Red River north and east of Hanoi as well as at Nam Du should be established, as this may provide important experiences for use in the Red River delta and other As-affected deltas.

## 6.4 Household-based water treatment

The As mitigation in areas where people are not covered by a centralized water supply, such as rural areas, is clearly more challenging. Firstly, a continuous effort to make people aware of the possible As contamination of their drinking water and the benefits of using aeration and sand filtration is encouraged. In all cases, filtration lowers the As concentration, and in many cases, the As concentration in the treated water will be below the guideline limit. The information can be distributed via television, posters at markets, and/or more directly in campaigns to individual local communities or households. Sand filtration in the Red River delta is accepted and used by many households already, posing a huge advantage for the introduction of new technologies. Specific recommendations (including an illustrated flyer) for sand filter promotion and optimization are presented in a report from EAWAG/CETASD (Luzi et al., 2004).

Secondly, if rural areas with a low groundwater Fe/As/P ratio can be identified these should be subject to an extraordinary mitigation effort. Even in such areas sand filtration will lower the As concentration and possibly oxidize As, and hence provide an important pre-treatment. Subsequent treatment will, however, be necessary. HWT units such as the SONO or the Kanchan filter are recommended in the Red River delta, especially as community-based treatment plants may be difficult to implement and maintain (Hossain et al., 2005). The SONO filter was developed for the As-affected areas in the Bengal delta where a low groundwater $R_{\mathrm{Fe/As/P}}$ value can be found (c.f., Hug et al., 2008).

## 6.5 Blanket testing of As levels in drinking water

Importantly, many of the above immediate mitigation actions may be taken without testing each individual tube well and/or treated drinking water for As. However, such testing should be part of the continuing mitigation action. If field tests are preferred, the As level can be determined reasonably precisely with careful sampling and analysis using the Wagtech digital Arsenator (UNICEF,

2008) or the Hach or Merck test kits used in previous surveys in the Red River delta (IET and VAST, 2004; Rosenboom, 2004). Safe and unsafe drinking water supplies may then be painted green or red, respectively, or households with an unsafe drinking water As level may be provided with an HWT unit.

## 6.6 Mitigation of As exposure via food

Surface water should continue to be used for irrigation to secure a low As-intake via food (c.f., Brammer, 2009). Additional advantages of irrigation by surface water are apparent. Firstly, the use of surface water for irrigation minimizes potential overexploitation of the groundwater, which is currently challenging the Hanoi water supply (Giger et al., 2003; Berg et al., 2008). Secondly, fresh groundwater is sparse in some areas with high groundwater salinity, including some areas with safe groundwater As concentrations (Jessen et al., 2008). In these areas utilization of fresh groundwater for irrigation may lead to an increased groundwater salinity, and hence ultimately force people to shift from safe groundwater to fresh surface water resources contaminated by pathogens and possibly pesticides (Giger et al., 2003).

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# 8 Appendices

**I** Postma D., Larsen F., Nguyen T. M. H., Mai T. D., Pham H. V., Pham Q. N. and Jessen S. (2007) Arsenic in groundwater of the Red River floodplain, Vietnam: Controlling geochemical processes and reactive transport modeling. Geochim. Cosmochim. Acta 71, 5054–5071.

**II** Larsen F., Pham Q. N., Dang, D. N., Postma D., Jessen S., Pham H. V., Nguyen B. T., Duc T. H., Luu T. T., Nguyen H., Chambon J., Nguyen V. H., Hoang D. H., Nguyen T. M. H., Mai T. D. and Refsgaard J. C. (2008) Controlling geological and hydrogeological processes in an arsenic contaminated aquifer on the Red River flood plain, Vietnam. Appl. Geochem. 23, 3099–3115.

**III** Jessen S., Larsen F., Postma D., Pham H. V., Nguyen T. H., Pham Q. N., Dang D. N., Mai T. D., Nguyen T. M. H., Duc T. H., Luu T. T., Hoang D. H. and Jakobsen R. (2008) Palaeo-hydrogeological control on groundwater As levels in the Red River delta, Vietnam. Appl. Geochem. 23, 3116–3126.

**IV** Postma D., Jessen S., Nguyen T. M. H., Mai T. D., Koch C. B., Pham H. V., Pham Q. N. and Larsen F. Mobilization of arsenic and iron from Red River floodplain sediments, Vietnam. Submitted to *Geochim. Cosmochim. Acta.*

**V** Jessen S., Postma D., Larsen F., Pham Q. N., Le Q. H., Tran V. L., Pham H. V. and Jakobsen R. The mobility of arsenic in a Red River floodplain aquifer: Results of a forced gradient experiment and surface complexation modelling. Manuscript.

The papers are not included in this www-version but may be obtained from the library at DTU Environment, Miljoevej, Building 113, Technical University of Denmark, DK-2800 Kgs. Lyngby (library@env.dtu.dk).

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