# Redox buffering and de-coupling of arsenic and iron in reducing aquifers across the Red River Delta, Vietnam, and conceptual model of de-coupling processes

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## Abstract

Analysis of over 500 groundwater samples from throughout the Red River Delta indicate de-coupling of dissolved arsenic (As) and dissolved iron (Fe). The sorting of all data along the redox potentials suggest re-adsorption of As released initially from Mn(IV)-oxyhydroxides and later from Fe(III)-oxyhydroxides on remaining ferric phases at moderate redox levels. Gradually decreasing specific surface available for re-adsorption of As probably plays a role as consequence of limited reactivity of more crystalline phases such as goethite and hematite. At low redox levels concentrations of Fe and phosphate decrease, but As concentration still keeps increasing. Based on the results of speciation modeling, there is supersaturation with respect to siderite and vivianite. A general conceptual model of As and Fe behaviour is presented, suggesting that coupled behaviour is possible in two windows, i.e. between saturation of remaining adsorption sites and the onset of siderite and vivianite precipitation and then after the beginning of secondary sulphide phases precipitation and during methanogenesis. Our large dataset demonstrates that formation of siderite and vivianite is a key factor in the de-coupling. The de-coupling of As from Fe is common and was observed at many sites around the world where As is released as a consequence of redox processes, e.g. in Bangladesh, West Bengal and Assam in India, the Mekong Delta in Cambodia and Vietnam, and Taiwan. The presented general conceptual model of de-coupling processes can be applied to the interpretation of As and Fe data, and, thus, it can help in the preparation of a site conceptual model which is a necessary prerequisite for reactive transport modeling.

## Introduction

Arsenic is a contaminant of serious environmental concern around the world. There are four principal processes responsible for arsenic release (Ravenscroft et al., 2009): reductive dissolution of ferric minerals, e.g. in Bangladesh, West Bengal in India, Cambodia, and Taiwan; alkaline desorption, e.g. the Chaco-Pampean region of Argentina and the West of the USA; oxidation of sulphides, e.g. New England and Wisconsin in the USA; and geothermal interactions, e.g. Central Mexico and New Zealand.

However, reductive dissolution of ferric minerals is by far the most important process because it affects large populations, e.g. in the Bengal Delta Plain and various regions in China and Southeast Asia (Refs). The process belongs to the sequence of primary redox reactions, PRR (Hunter et al., 1998; Appelo and Postma, 2005), in which electron acceptors react gradually with organic matter as follows: (1) consumption of oxygen, (2) nitrate reduction, (3) Mn(IV) reduction, (4) Fe(III) reduction, (5) sulphate reduction, and (6) methanogenesis. Due to the heterogeneity of aquifers, an overlap of redox zones and a simultaneous consumption of several electron acceptors has often been observed (Jacobsen and Postma, 1999, Christensen et al., 2000; Vencelides et al., 2007, Mukherjee et al., 2008). Depending on the pH value and the sulphate/Fe(III) ratio, bacteria may favour sulphate over Fe as terminal electron acceptor (redox buffer) (Postma and Jakobsen, 1996).

In situations when concentrations of specific electron acceptors are low, some steps in the redox sequence are skipped. An example is the Bemidji site in Minnesota, USA, contaminated by petroleum hydrocarbons, where principal redox reactions after depletion of oxygen are Fe(III) reduction and methanogenesis (Essaid et al., 2011). At this site, concentration of As in a petroleum hydrocarbon plume is up to 230 µg/L as a consequence of As release from ferric hydroxides in reducing environment and drops to less than 5 µg/L at the aerobic leading edge of the plume where arsenic is adsorbed and co-precipitates with the re-precipitated ferric minerals (Cozzarelli et al., 2016).

Primary redox processes can be followed by secondary reactions, when previously released products of PRR interact and are transferred from aqueous to solid phase (Hunter et

al., 1998). Principal secondary reactions are (1) precipitation of rhodochrosite ($MnCO_3$), (2) precipitation of siderite ($FeCO_3$), and precipitation of amorphous sulphides such as mackinawite ($FeS$). At As-contaminated sites, the lack of correlation between dissolved Fe and As is frequently observed, e.g. Hasan et al. (2007) and this was generally interpreted as a consequence of the SRR.

The Red River Delta in Northern Vietnam is a densely populated area where groundwater has been pumped for the Hanoi public water supply for more than 100 years. Some 65% of the groundwater wells exceed the WHO limit for As and/or other trace elements such as e.g. manganese (Winkel et al., 2011). The area comprises sediments of Pleistocene and Holocene age, the latter deposited by postglacial marine transgression (Berg et al., 2008). There were extensive studies of As contamination in both local and regional scale, e.g. Postma et al. (2007), Larsen et al. (2008), Eiche et al. (2008), Winkel et al. (2011), van Geen et al. (2013), and Mai et al. (2014). In all studies the importance of reductive dissolution of ferric oxyhydroxides has been recognized and the colouring of the sediments was suggested as a proxy for redox status determination, just like in Bangladesh (von Brömssen et al., 2007). Generally low correlation between dissolved Fe and As was interpreted as a consequence of ferrous minerals precipitation. Most As dissolved in groundwater was As(III) and the reactivity of iron oxides in river sediments was relatively low and decreased from lepidocrocite to hematite (Postma et al., 2010).

In this study we aimed to elucidate low correlation between dissolved Fe and As frequently found in As-contaminated aquifers (see later) and observed partial overlap in redox reactions. Since the de-coupling of Fe and As was observed at many other sites, we compare the Red River delta with other arsenic-contaminated sites in the world. The comparison is based on sampling from long screen wells and has to be interpreted with caution, but we believe there are meaningful patterns that can be deduced.
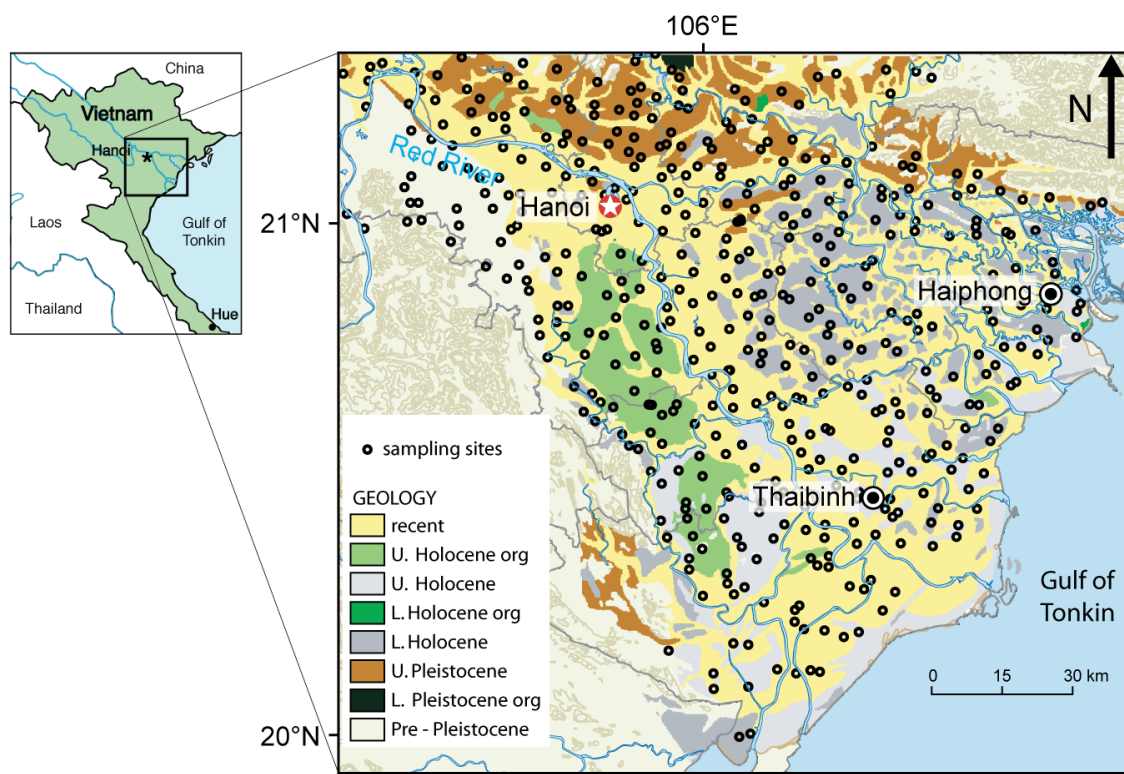
Fig. 1. Map of sampling sites in the Red River Delta, data from Winkel et al., 2011. (Figure near here)

## Material and Methods

Samples of groundwater were collected from 512 pumped wells (Fig. 1). Temperature, pH, redox potential and electrical conductivity were measured in the field using the portable systems YSI 556 and WTW Multi 340i. Readings of redox potentials were normalized to the standard hydrogen electrode with the T-corrected standard potential of the Ag/AgCl reference electrode. The samples were collected in polypropylene bottles pre-rinsed with $HNO_3$. A filtered aliquot of 60 mL was acidified with $HNO_3$ to pH < 2 and used for the determination of major anions and cations, ammonium, phosphate, metals and metalloids. Anions, alkalinity, and DOC were determined from non-acidified and unfiltered samples.

Major cations, Fe and Mn were determined by ICP-OES. Sulphate and chloride were determined by chromatography (Dionex), phosphate by photometry, alkalinity by titration with HCl using Gran plot analysis to determine the titration end point, and DOC was determined with a TOC 5000 A analyser (Shimadzu).

Arsenic was analysed in parallel by atomic fluorescence spectroscopy (AFS, Millennium Excalibur, PS Analytical) and high resolution HR ICP-MS (Element 2, Thermo Fisher). The quantification limit for arsenic was 1 μg/L. The precision of analytical results was ±5%. More information about sampling and analyses is in Berg et al. (2008).

The program ChemEQL (Müller, 2015; http://www.eawag.ch/en/department/surf/projects/chemeql/) was used for speciation calculations. Saturation indices (SI) were calculated as the logarithm of the ratio $Q/K_{sp}$ (Stumm and Morgan, 1996), hence, a positive SI indicates oversaturation and a negative SI undersaturation. Earlier, the program has been tested against the standard Phreeqc code (Parkhurst and Appelo, 1999) and results of calculations were mutually consistent.

## Results

### Water chemistry

Groundwater chemistry and As speciation

Groundwater is of Ca-Mg-HCO$_3$ type and evolves locally towards Na-Cl type (Berg et al., 2008). Values of pH are from slightly acidic to alkaline. Values of Eh are from +6 mV to +710 mV, i.e. covering a wide range from reducing to oxidizing conditions, but well above sulphate reduction and As(V) reduction. Anaerobic conditions predominated in the majority of samples. Maximum As concentration is 427 μg/l, minimum is below detection limit of 0.1 μg/l, average is 22.3 μg/l.

The complete dataset can be found in Winkel et al. (2011). Analytical speciation of arsenic was available only for selected samples and is presented in Eiche et al. (2008). In samples with As concentration more than 10 μg/l As(III) comprises more than 90% of the total arsenic, in samples with less than 10 μg/l of arsenic As(III) comprises between 50 and 90% of the total arsenic.

Dissolved Fe and As correlations

There is an evident de-coupling between dissolved Fe and As with values of Person's correlation coefficient r = 0.051.Also, correlation between dissolved Mn and As is weakly

negative with r = −0.057. In fact, none samples with elevated Mn concentrations (dissolved Mn more than 2.4 mg/l) have As concentration more than 90 µg/l, i.e., high dissolved Mn concentrations and high dissolved As concentrations are mutually exclusive.

Effect of redox potentials on elemental concentrations

To clarify the relation among dissolved of As and concentrations of indicator redox species, moving averages of their concentrations normalized to maximum concentrations of each species were plotted in Fig. 2 (top) as a function of redox potential with respect to standard hydrogen electrode (SHE). Concentrations of Mn slightly decrease first at Eh values around +450 mV, but then they increase again before finally decreasing at about +200 mV. Concentrations of sulphate also fluctuate and decrease to low levels at about +200 mV. Concentrations of Fe start to increase at about +250 mV, reach a maximum at about +175 mV and then decline steadily (Fig. 2, bottom). Concentrations of phosphate begin to increase at about +190 mV, reaching a maximum at about +85 mV and then decline. Finally, As concentrations also start to increase significantly at about +100 mV, reaches a maximum at +75 mV, but they seem to decrease at lower Eh values (Fig. 2, bottom). In contrast, phosphate concentrations, initially increasing in parallel to As, decrease at the low redox level, suggesting a sink for dissolved phosphate. Concentrations of $HCO_3$ and Ca are high at Eh around +100 mV, Fig. 2 (bottom), and then decrease.
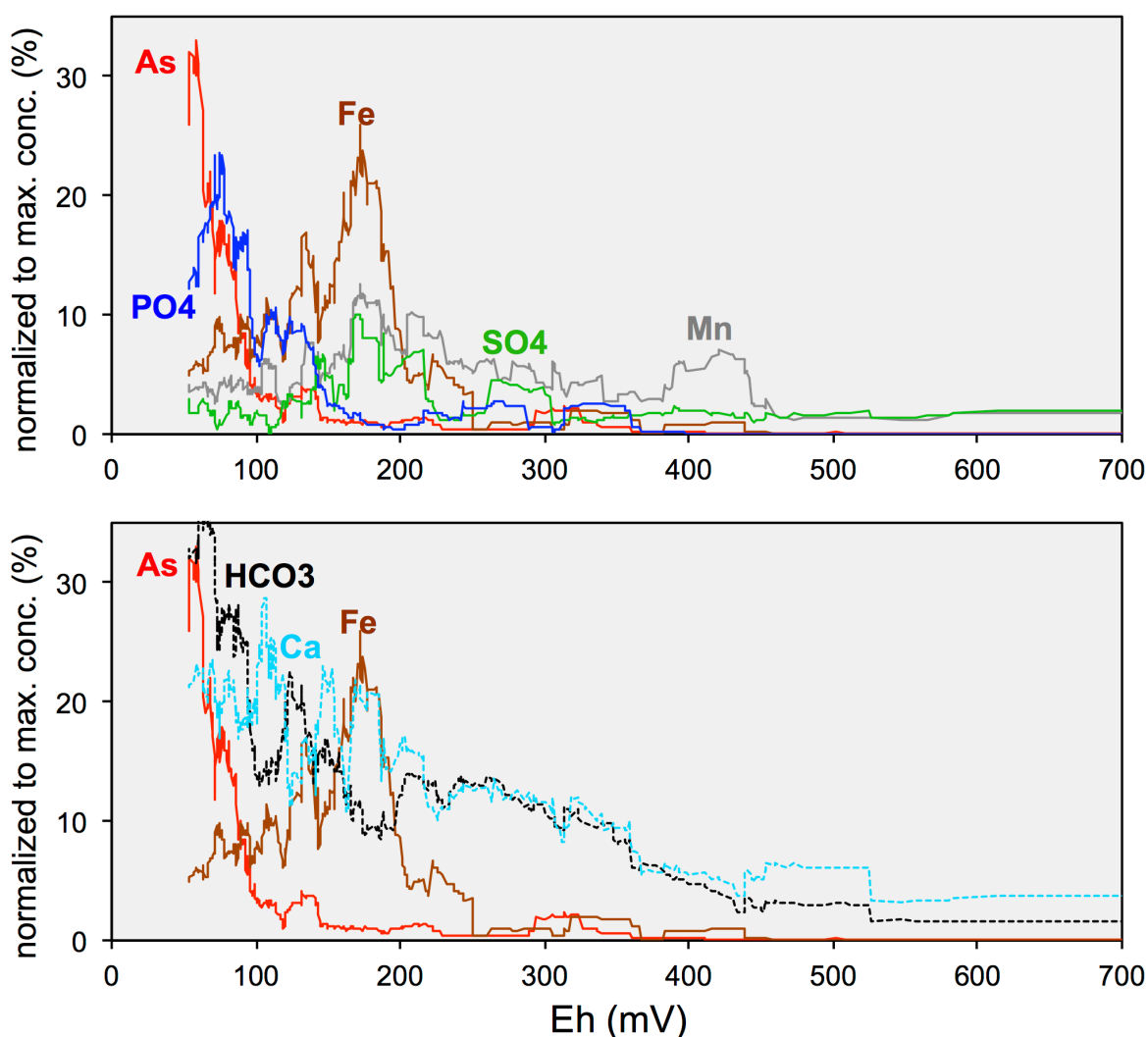
Fig. 2. Plot of normalized redox indicator concentrations as a function of redox potential. Concentrations of the individual species were normalized with regard to their maximum concentration and smoothed, using a moving average filter with a period of 25. (near here)

Speciation modeling

The supersaturation with respect to the solid phase minerals goethite, vivianite, siderite, and calcite was tested using the activities of the solution composition and $E_H$-values for all individual samples. The SI values as a function of redox potentials are depicted in Figure 3. Undersaturation with respect to goethite begins at $E_H$ of about 380 mV and SI values seem to be almost constant from Eh of about 250 mV. Groundwater becomes supersaturated with respect to vivianite at $E_H$ below +130 mV and reaches maximum values at +85 mV and

then remains high. The onset of siderite precipitation begins below +95 mV and supersaturation reaches maximum at $E_H$ of +50 mV. Supersaturation with respect to calcite was just about to start at +50 mV. Supersaturation with respect to Mn(II), (III), (IV) or S(-II) phases (not shown here) was not observed in the present pH-pɛ range, which agrees with corresponding Pourbaix diagrams (e.g. Stumm and Morgan, 1996).
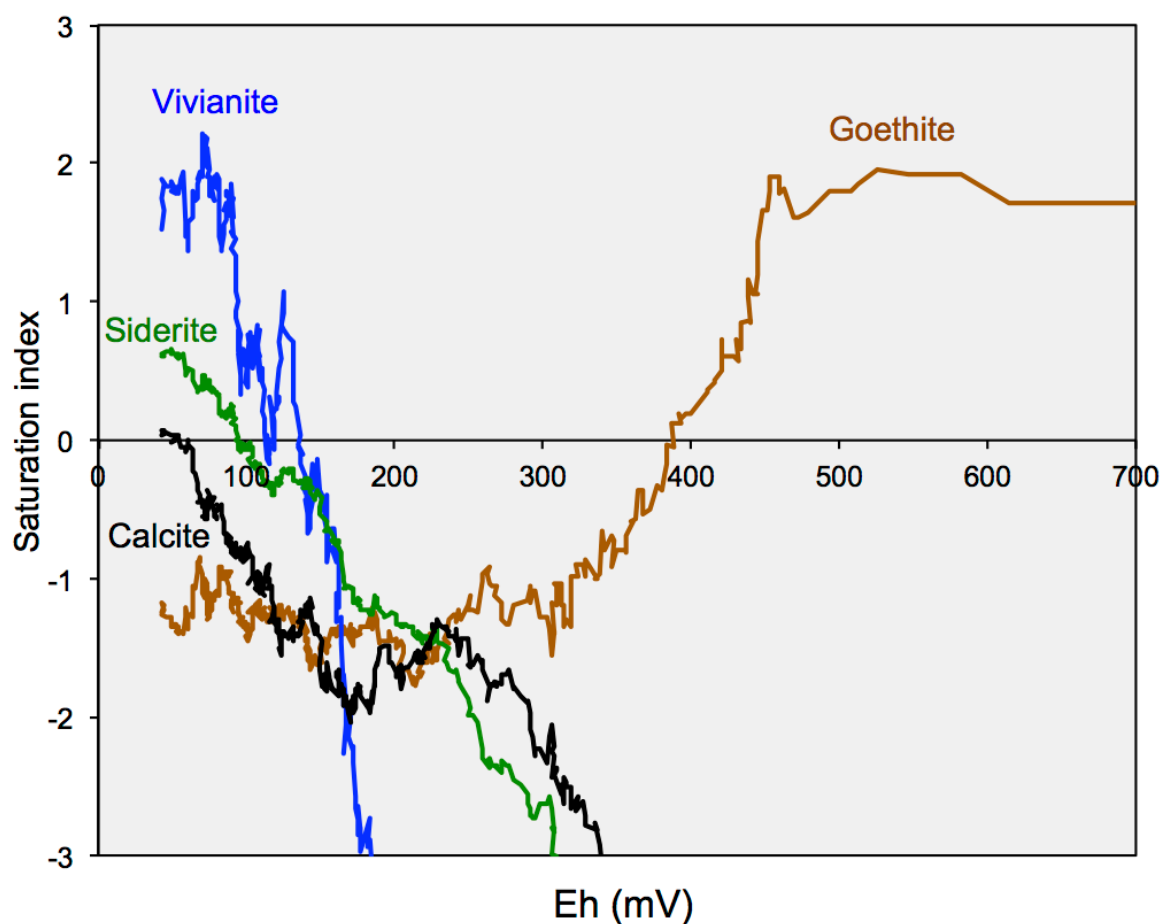


Fig. 3. Selected saturation indices (SI) for groundwater samples from the Red River Delta. The line was smoothed with a running average of 25 samples. (near here)

## Discussion

### De-coupling at the Red River Delta site

In our data set (Figure 2), there is a shift of about 100 mV between Fe and As maxima, indicating that As concentration increases significantly when Fe concentration decreases to a

relatively low level. However, phosphate is also de-coupled from Fe and partly also from As, when redox levels become very low. De-coupling of As from Fe was observed in batch experiments with acetate as an electron donor (Islam et al., 2004). Release of As took place after Fe(III) reduction and it was interpreted as a consequence of slower As(V) to As(III) reduction and delayed release of As(III) with lower adsorption affinity.

The most plausible explanation of the de-coupling, observed at the Red River delta at intermediate to low redox level conditions, is the concept of As re-adsorption presented by McArthur et al. (2004). Reduction of Mn(IV)-oxyhydroxides is favoured thermodynamically and released As is re-adsorbed on still stable Fe(III)-oxyhydroxides. When there is reduction in progress, dissolved Fe concentrations increase, but released As is again re-adsorbed on remaining ferric phases. Only when a small fraction of initial Fe(III)-oxyhydroxides is left, saturation of remaining adsorption sites is reached and there is a relatively fast build-up of As concentration in groundwater (McArthur et al., 2004). This is further facilitated by dominant As(III), which has a lower adsorption affinity than As(V). Different reactivity of Fe(III) minerals also seems to play a role. In extraction experiments performed on Red River Delta samples and using ascorbic acid, Postma et al. (2010) found that Fe(III) mineral reactivity decreased in the order from lepidocrocite to poorly crystalline goethite to hematite. It seems that poorly crystalline phases such as ferrihydrite with the largest surface area dissolve first and, thus, the specific surface available for As re-adsorption and reaction decreases during the reductive dissolution progress.

Concentrations of Fe and PO4 were also observed to decrease during the reduction phase. Assuming conservative behaviour of both species, their concentrations should be fairly constant after complete dissolution of ferric phases, but this is not observed. A possible explanation is in precipitation of siderite, $FeCO_3$, and vivianite, $Fe_3(PO_4)_2.8H_2O$ (Sracek et al., 2004). Precipitation of siderite is consistent with positive saturation indices for siderite (Jessen et al., 2008; Eiche et al., 2008). Furthermore, precipitated secondary minerals like siderite may be coating the surface of Fe(III)-oxyhydroxides, further limiting their dissolution (Vencelides et al., 2007). In fact, coatings formed by Fe(II) or mixed Fe(II/III) phases corresponding to siderite, vivianite or magnetite were found in Bangladesh by Horneman et al. (2004).

**General conceptual model of de-coupling processes**

The general conceptual model of As mobilization, which goes beyond saturation of remaining adsorption sites presented in the model of McArthur et al. (2004), and inspired by the Red River Delta data and which is considered applicable to other sites of groundwater arsenic enrichment in the world, is shown in Fig. 4. Sulfate reduction and methanogenesis are also included since these processes were reported to occur in the Red River Delta (Postma et al. 2007; van Geen et al. 2013) and other regions like the Bengal Delta Plain (BDP). After the consumption of oxygen and $NO_3$, most MnOOH in the solid phase dissolves and the reduction of Fe(III) phases begins. Concentrations of dissolved Fe increase, but concentration of dissolved As remain low because released As is re-adsorbed by the remaining Fe(III) phases (McArthur et al. 2004). Only when a small fraction of FeOOH remains, and all adsorption sites become saturated, can concentrations of dissolved As increase (segment 1 in Fig. 4), and thus, the behaviour of Fe and As then becomes coupled. In the meantime, the rate of Fe(III) mineral dissolution decreases because only the most resistant phases (goethite, hematite) are left behind in the solid phase. When supersaturation with respect to siderite (and perhaps also vivianite) is reached, Fe is scavenged from water, but As remains mobile. When the redox levels drop further, sulfate is reduced and secondary sulfide phases such as mackinawite precipitate which scavenges both Fe and As, i.e., their removal occurs simultaneously at this phase and both species are coupled (segment 2a in Fig. 4). Finally, methanogenesis begins under very reducing conditions and concentrations of Fe and As start to increase in parallel again, assuming there is still some ferric iron left in the solid phase (segment 2b in Fig. 4). At this stage, precipitation of siderite may become less significant because a large portion of DIC is converted to methane.
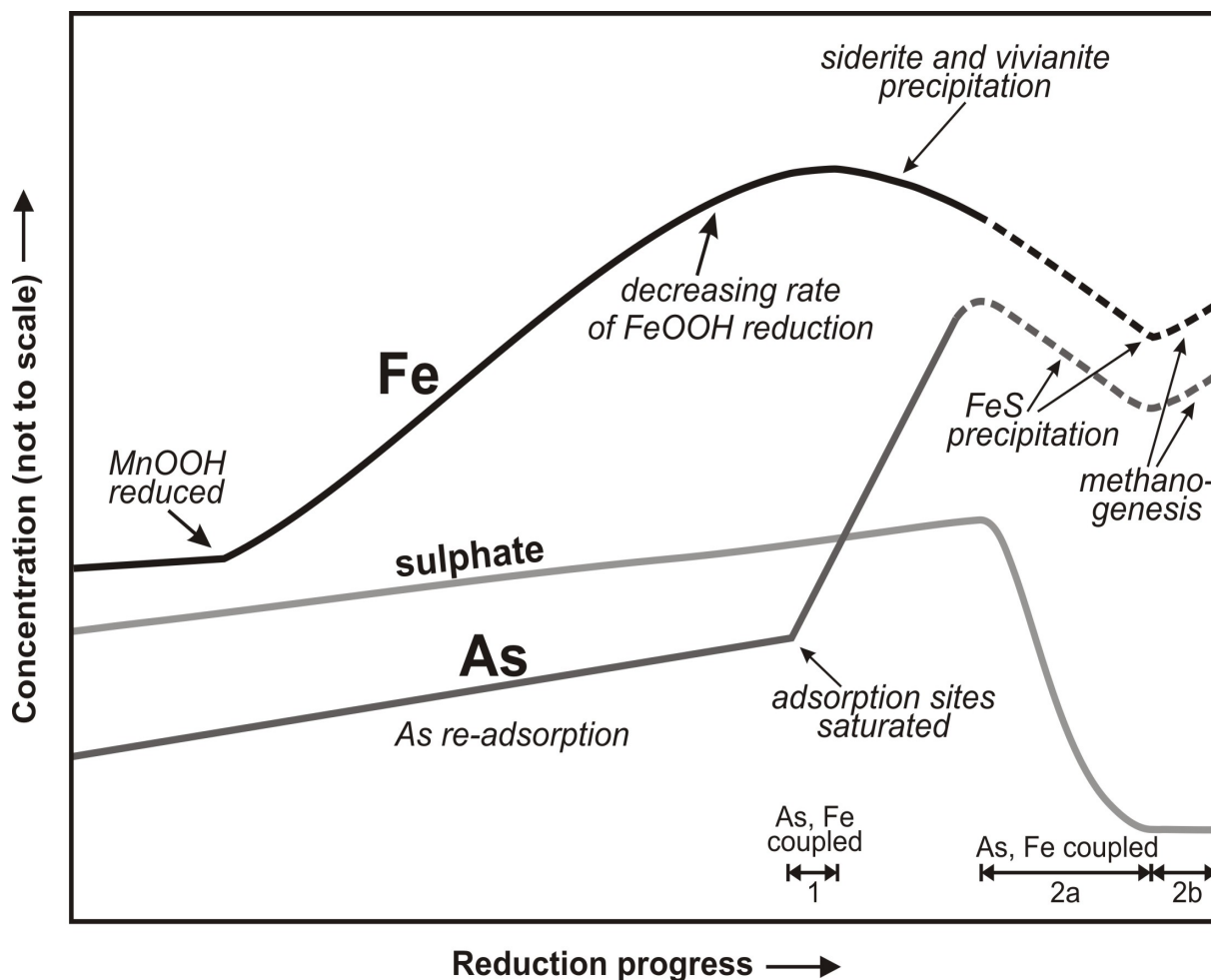
Fig. 4. Conceptual model of As behaviour: First, the As and Fe coupling window is between saturation of adsorption sites and precipitation of siderite (segment 1), the second window starts after the onset of sulphide precipitation (segment 2a) and during methanogenesis (segment 2b).   (near here)

In summary, based on the presented conceptual model, a coupled Fe and As behavior is possible between the saturation of adsorption sites and the beginning of siderite and vivianite precipitation, i.e., in a relatively narrow redox range. A second window of the coupled As and Fe behavior (both concentrations are decreasing) is after the onset of secondary sulfide precipitation (assuming that the redox level of sulfate reduction is reached and that secondary sulfide incorporates As) and later during methanogenesis.

The lack of correlation between dissolved As and Fe is rather a rule than an exception world-wide (Table 1). It has been observed at many sites where reductive dissolution of ferric minerals is a principal process of As release, e.g. in Bangladesh, West Bengal and Assam in India, and Taiwan. These sites have several common characteristics: (a) Reducing conditions sometimes reaching the level of methanogenesis, (b) very low or below detection limit concentrations of oxygen, nitrate and sulphate, (c) high concentrations of DOC, ammonia and phosphate, and (d) high concentrations of dissolved Fe and Mn. A common feature of all sites is supersaturation with respect to siderite and, to a limited extent, with respect to vivianite (e.g., Ravenscroft et al., 2005; Hasan at al., 2007). Precipitation of sulphidic phases such as mackinawite was also confirmed at some sites, e.g., framboidal authigenic pyrite has been found by Nickson et al. (2000) in Bangladesh. High As concentrations were observed in the Mekong Delta in Cambodia under methanogenic conditions, but As concentrations were much lower under sulphate-reducing conditions (Buschmann and Berg, 2009; Buschmann et al., 2007, 2008).

Table 1. Relation between As and Fe at world sites with reductive dissolution As release (near here)

| Site | Correlation As/Fe | Positive SI for siderite | Comment | Source |
|---|---|---|---|---|
| Bangladesh | moderate | n.a. | Initial study | Nickson et al., 2000 |
| Bangladesh | moderate | Yes | Review study | Ahmed et al., 2004 |
| Bangladesh | low | Yes | Comparative study | Hasan et al., 2007 |
| Cambodia, Mekong Delta | low | Yes | Initial study | Buschmann et al. 2007 |
| Sonargaon, Bangladesh | low | Yes | Comparative study | Bhattacharya et al., 2009 |
| Chandina, Bangladesh | low | Yes | Comparative study | Bhattacharya et al., 2009 |
| Sirajdikhan, Bangladesh | low | Yes | Comparative study | Bhattacharya et al., 2009 |
| Bhagirathi, West Bengal | moderate | Yes | Comparative study | Maity et al., 2011 |
| Padma/Meghna, Bangladesh | moderate | Yes | Comparative study | Maity et al., 2011 |

| Barasat, West Bengal | moderate | n.a. | | McArthur et al., 2004 |
|---|---|---|---|---|
| Matlab, Bangladesh | low | Yes | Sediment colour study | von Brömssen et al., 2007 |
| Assam, India | low | Yes | Regional study | Mahanta et al., 2015 |
| Chakdaha, India | moderate | Yes | | Nath et al., 2008b |
| Chianan, Taiwan | low | Yes | | Nath et al., 2008a |
| Chianan, Taiwan | low | Yes | Comparative study | Maity et al., 2011 |
| Chianan, Taiwan | moderate | Yes | Zonal and mud volcanos study | Sengupta et al., 2014 |
| Lanyang, Taiwan | moderate | Yes | Comparative study | Maity et al., 2011 |
| Vietnam, Mekong Delta | low | Yes | Initial study | Buschmann et al. 2008 |

n.a. – not available

## Conclusions

An extensive data set of groundwater analyses from the Red River delta was used to determine the sequence of redox buffering and processes responsible for As and Fe behaviour. Redox indicators show a strong de-coupling of dissolved As from Mn and Fe behaviour. It can be interpreted as re-adsorption of As released initially from Mn(IV)-oxyhydroxides and later from Fe(III)-oxyhydroxides on remaining ferric phases. The release of As begins after saturation of adsorption sites. Gradually decreasing specific surface available for re-adsorption of As probably plays a role as a consequence of limited reactivity of more crystalline phases such as goethite and hematite. Even at very low redox levels, concentrations of Fe and phosphate decrease, but As concentration still increases. This seems to be a consequence of siderite and vivianite precipitation.

We suggested a conceptual model inspired by the Red River data and also other sites with reductive dissolution of ferric oxyhydroxides. The model aims to explain the relation between saturation of remaining adsorption sites and the precipitation of secondary ferrous minerals and methanogenesis.

Based on the presented conceptual model of As and Fe behaviour at sites with As-enrichment, their coupled behaviour is possible at two redox windows between saturation of remaining adsorption sites and the onset of siderite and vivianite precipitation, and then after the beginning of secondary sulphides precipitation followed by methanogenesis. De-coupling of As from Fe was observed at many sites around the world where As is released to groundwater as a consequence of reductive dissolution including Bangladesh, West Bengal and Assam in India, Cambodia, China, and Taiwan. Processes responsible for de-coupling such as saturation of remaining adsorption sites and precipitation of minerals such as siderite and mackinawite should be implemented in conceptual model of As-contaminated sites and then in reactive transport models used for the prediction of arsenic behavior.

# References

Ahmed, K.M., Bhattacharya, P., Hasan, M.A., Akhter, S.H., Alam, S.M.M., Bhuyian, M.A., Imam, M.B., Khan, A.A., Sracek, O., 2004. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: An overview, Applied Geochemistry, Vol. 19, No. 2, 181-200.

Appelo, C.A.J, Postma, D., 2005. Geochemistry Groundwater and Pollution, 2nd Edition, A.A. Balkema Publishers, 649 p.

Berg, M., Trang, P.T.K., Stengel, C., Buschmann, J., Viet, P.H., Dan, N.V., Giger, W., Stuben, D., 2008. Hydrological and sedimentary controls leading to arsenic contamination of groundwater in the Hanoi area, Vietnam: The impact of iron-arsenic ratios, peat, river bank deposits, and excessive groundwater abstraction, Chem. Geol. 249, 91-112.

Bhattacharya, P., Hasan, M.A., Sracek, O., Smith, E., Ahmed, K.M., Brömssen von, M., Huq, S.M.I., Naidu, R., 2009. Groundwater chemistry and arsenic mobilization in the Holocene flood plains in south-central Bangladesh, Envir. Geochem. Health, 31, 23-43.

Buschmann, J., Berg, M., Stengel, C., Sampson, M.L., 2007. Arsenic and Manganese Contamination of Drinking Water Resources in Cambodia: Coincidence of Risk Areas with Low Relief Topography. Environ. Sci. Technol. 41, 2146-2152.

Buschmann, J., Berg, M., Stengel, C., Winkel, L., Sampson, M.L., Trang, P.T.K., Viet, P.H., 2008. Contamination of Drinking Water Resources in the Mekong Delta Floodplains: Arsenic and Other Trace Metals Pose Serious Health Risks to Population. Environ. Int. 34, 756–764.

Buschmann, J., Berg, M., 2009. Impact of sulfate reduction on the scale of arsenic contamination in groundwater of the Mekong, Bengal and Red River deltas, Appl. Geochem. 24, 1278-1286.

Christensen, T.H., Bjerg, P.L., Banwart, S.A., Jakobsen, R., Heron, G., Albrechtsen, H.-J., 2000. Characterization of redox conditions in groundwater contaminant plumes. J. Contam. Hydrol. 45, 165–241.

Cozzarelli, I.M., Schreiber, M.E., Erickson, M.L., Ziegler, B.A., 2016. Arsenic Cycling in Hydrocarbon Plumes: Secondary Effects of Natural Attenuation, Groundwater 54, 1, 35-45.

Eiche, E., Neumann, T., Berg, M., Weinmann, B., van Geen, A., Norra, S., Berner, Z., Trang, P.T.K., Viet, P.H., Stüben, D., 2008. Geochemical processes underlying a sharp contrast in groundwater arsenic concentrations in a village on the Red River delta, Vietnam, Appl. Geochem. 23, 3143-3154.

Essaid, H.I., Bekins, B.A., Herkelrath, W.N., Delin, D.N., 2011. Crude oil at the Bemidji site: 25 years of monitoring, modeling, and understanding, Ground Water 49, 5, 706-726.

Hasan, M.A., Ahmed, K.M., Sracek, O., Bhattacharya, P., Brömssen von, M., Broms, S., Fogelström, J., Mazumder, M.L., Jacks G., 2007. Arsenic in shallow groundwater of Bangladesh: investigation from three different physiographic settings, Hydrogeology Journal, 15, 1507-1522.

Horneman, A., van Geen, A., Kent, D.V., Mathe, P.E., Zheng, Y., Dhar, R.K., O'Conell, S., Hoque, M.A., Aziz, Z., Shamsudduha, M., Sediqque, A.A., Ahmed, K.M., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part I: Evidence from sediment profiles, Geochim. Cosmochim. Acta 68, 17, 3459-3473.

Hunter, K.S., Wang, Y., Van Cappellen, P., 1998. Kinetic modeling of microbially-driven redox chemistry of subsurface environments: coupling transport, microbial metabolism and geochemistry. J. Hydrol. 209, 56–80.

Islam, S.I., Gault, A.G., Bootham, C., Polya, D.A., Charnock, J.M., Chaterjee, D., Lloyd, J.R., 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments, Nature 430, 68-71.

Jakobsen, R., Postma, D., 1999. Redox zoning, rates of sulfate reduction and interaction with Fe-reduction and methanogenesis in a shallow sandy aquifer, Romø, Denmark. Geochim. Cosmochim. Acta 63 (1), 137–151.

Jessen, S., Larsen, F., Postma, D., Viet, P.H., Ha, N.T., Nhan, P.Q., Nhan, D.D., Duc, M.T., Hue, N.T.M., Huy, T.D., Luu, T.T., Ha, D.H., Jakobsen, R., 2008. Paleohydrological control on groundwater As levels in Red River delata, Vietnam, Appl. Geochem. 23, 3116-3126.

Larsen, F., Pham, N.Q., Dang, N.D., Postma, D., Jessen, S., Pham, V.H., Nguyen, T.B., Trieu, H.D., Tran, L.T., Nguyen, H., Chambon, J., Nguyen, H.V., Ha, D.H., Hue, N.T., Duc, M.T., 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.

Mahanta, C., Enmark, G., Nordborg, D., Sracek, O., Nath, B., Nickson, R.T., Herbert, R., Jacks, G., Mukherjee, A., Ramanathani, A.L., Bhattacharya, P., 2015. Groundwater arsenic in the Holocene Brahmaputra floodplains of Assam, Northeastern India: distribution, hydrogeochemistry and mobilization mechanism, J. Hydrol., Region. Stud., in press.

Mai, N.T.H., Postma, D., Trang, P.T.K., Jessen, S., Viet, P.H., Larsen, F., 2014. Adsorption and desorption of arsenic to aquifer sediment on the Red River fllodplain at Nam Du, Vietnam, Geochim. Cosmochim. Acta 142, 587-600.

Maity, J.P., Nath, B., Chen, C.-Y., Bhattacharya, P., Sracek, O., Bundschuh, J., Kar, S., Thunvik, R., Chatterjee, D., Ahmed, K.M., Jacks, G., Mukherjee, A.B., Jean, J.-S., 2011. Arsenic-enriched groundwaters of India, Bangladesh and Taiwan-Comparison of

hydrochemical characteristics and mobility constraints, J. Environ. Sci. Health, Part A, 46: 11, 1163-1176.

McArthur, J.M., Bannerjee, D.M., Hudson-Edwards, K.A., Mishra, R., Purohit, R., Ravenscroft, P., Cronin, A., Howarth, R.J., Chatterjee, A., Talukder, T., Lowry, D., Houghton, S., Chadha, D.K. 2004. Natural organic matter in sedimentary basins and relation to arsenic in anoxic groundwater: the example of West Bengal and its worldwide implications. Appl.Geochem. 19,1255–1293.

Mukherjee, A., Brömssen von, M., Scanlon, B., Bhattacharya, P., Fryar, A.E., Hasan, M.A., Ahmed, K.M., Chatterjee, D., Jacks, G., Sracek, O., 2008. Hydrogeochemical comparison and effects of overlapping redox zones on groundwater arsenic near the Western (Bhagirathi sub-basin, India) and Eastern Margins (Meghna sub-basin, Bangladesh) of the Bengal Basin, Journal of Contaminant Hydrology, 99, 1-4, 31-48.

Nath, B., Jean, J.S., Lee, M.K., Yang, H.J., Liu, C.C., 2008a. Geochemistry of high arsenic groundwater in Chia-Nan plain, Southwestern Taiwan: possible sources and reactive transport of arsenic. J. Contam. Hydrol. 99 85–96.

Nath, B., Stüben, D., Mallik, S.B., Chatterjee, D., Charlet, L., 2008b. Mobility of arsenic in West Bengal aquifers conducting low and high groundwater arsenic. Part I: Comparative hydrochemical and hydrogeological characteristics, Appl. Geochem. 23, 5, 977-995.

Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G., Ahmed, K.M., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal, Appl. Geochem. 15, 4, 403-413.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC; a Computer Program for Speciation, Reaction-path, 1-D Transport and Inverse Geochemical Calculations, U.S. Geological Survey Water Resources-Investigations Report 99-4259.

Postma, D., Jakobsen, R., 1996. Redox zonation: Equilibrium constraints on the Fe(III)/$SO_4$-reduction interface, Geochim. Cosmocim. Acta 60, 17, 3169-3175.

Postma, D., Larsen, F., Hue, N.T.M., Duc, M.T., Viet, P.H., Nhan, P.Q., 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.

Postma, D., Jessen, S., Hue, N.T.M., Duc, M.T., Koch, C.B., Viet, P.H., Nhan, P.Q., Larsen, F., 2010. Mobilization of arsenic and iron from Red River flodplain sediments, Vietnam, Geochim. Cosmochim. Acta 74, 3367-3381.

Ravenscroft, P., Burgess, W.G., Matin, K.M., Burren, M., Perrin, J., 2005. Arsenic in groundwater of the Bengal Basin, Bangladesh: Distribution, field relations, and hydrogeological setting, Hydrogeology J. 13, 727-751.

Ravenscroft, P., Brammer, H., Richards, K., 2009. Arsenic Pollution A Global Synthesis, Wiley-Blackwell, 588 p.

Rowland, H.A.L., Gault, A.G., Lythgoe, P., Polya, D.A., 2008. Geochemistry of aquifer sediments and arsenic-rich groundwaters from Kandal Province, Cambodia, Appl. Geochem. 23, 11, 3029-3046.

Sengupta, S., Sracek, O., Jean, J.-S., Lu, H.-Y., Wang, C.-H., Palcsu, L., Liu, C.-C., Jen, C.-H., Bhattacharya, P., 2014. Spatial variation of groundwater arsenic distribution in Chianan Plain, SW Taiwan: Role of local hydrogeological factors and geothermal sources, Journal of Hydrology 518, Part C, 393-409.

Sracek, O., Bhattacharya, P., Jacks, G., Gustafsson, J.P., Brömssen von, M., 2004. Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments, Applied Geochemistry, Vol. 19, No.2, 169-180.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry, 3$^{rd}$ Edition, New York: Wiley-Interscience.

Vencelides, Z., Sracek, O., Prommer, H., 2007. Modelling of iron cycling and its impact on the electron balance at a petroleum hydrocarbon contaminated site in Hnevice, Czech Republic, Journal of Contaminant Hydrology 89, 3-4, 270-294.

van Geen, A., Bostick, B.C., Kim Trang, P.T., Mai Lan, V., Hung Viet, P., Radloff, K., Aziz, Z., Mey, J.L., Stahl, M.O., Harvey, C.F., Oates, P., Weinman, B., Stengel, C., Frei, F., Kipfer, R., Berg, M., 2013. Retardation of arsenic transport through a Pleistocene aquifer, Nature 501, 204-207.

von Brömssen, M., Jakariya, M., Bhattacharya, P., Ahmed, K.M., Hasan, M. A., Sracek, O., Jonsson, L., Lundell, L., Jacks, G., 2007. Targeting low-arsenic aquifers in Matlab Upazila, Southeastern Bangladesh, Science of the Total Environment 379, 121-132.

Winkel, L.H.E., Trang, P.T.K., Lan, V.M., Stengel, C., Amini, M., Ha, N.T., Viet, P.H., Berg, M., 2011. Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer exploitation for more than a century, PNAS 108, 1246-1251.

## List of tables

Table 1. Relation between As and Fe at world sites with reductive dissolution As release.

## List of figures

Fig. 1. Map of sampling sites in the Red River Delta.

Fig. 2. Plot of normalized redox indicator concentrations as a function of redox potential. Concentrations of the individual species were normalized with regard to their maximum concentration and smoothed, using a moving average filter with a period of 25.

Fig. 3. Selected saturation indices for groundwater samples from the Red River Delta. The line was smoothed with a running average of 25 samples.

Fig. 4. Conceptual model of As behaviour: First, the As and Fe coupling window is between saturation of adsorption sites and precipitation of siderite (segment 1), the second window starts after the onset of sulphide precipitation (segment 2a) and during methanogenesis (segment 2b).