Supporting Information

Fate of arsenic during Red River water infiltration into aquifers beneath Hanoi, Vietnam.

Dieke Postma*¹, Nguyen Thi Hoa Mai², Vi Mai Lan², Pham Thi Kim Trang², Helle Ugilt Sø¹,

Pham Quy Nhan³, Flemming Larsen¹, Pham Hung Viet², Rasmus Jakobsen¹

¹Geological Survey of Denmark and Greenland, Øster Voldgade 10, DK-1350 Copenhagen, Denmark. ²Research Centre for Environmental Technology and Sustainable Development (CETASD), Hanoi University of Science (VNU), Hanoi, Vietnam.

Supporting Information contains five pages.

³Dept. of Hydrogeology, Hanoi University of Mining and Geology (HUMG), Hanoi, Vietnam. * corresponding author <u>diekepostma@gmail.com</u> phone +45 30273702

This annex shortly describes the application of the reactive transport model used in the present study. For a more complete presentation of the model, the reader is referred to Postma et al. (2016)¹. The model consists of a 1-D reactive transport model to be run in the code PHREEQC-3². It describes how the groundwater chemistry in arsenic contaminated aquifers on the Red River floodplain changes as a function of the burial age of the aquifer sediments. The key processes in the model are the degradation of sedimentary carbon and the reduction of As-containing Fe-oxides. Both components are consumed over time and become less reactive as well. Both processes are quantified by rate equations. For organic carbon the rate equation is:

$$-dC_{\rm C}/dt = m_{\rm o} \cdot 9.3 \cdot 10^{-12} \cdot (m_{\rm t}/m_{\rm o})^{2.5} \qquad ({\rm mol/sec})$$
(1)

Where $m_o = 1.36 \text{ mol/L}$ is the initial mass of organic C based on the analytical concentration 0.27 % C in the sediment, recalculated to the concentration per liter of contacting groundwater,¹, m_t , the mass of organic carbon at time t and $9.3 \cdot 10^{-12} \text{ sec}^{-1}$ the rate constant obtained by fitting the model to the field data. The exponent to (m_t/m_o) reflects the heterogeneity of the organic carbon reactivity and was likewise obtained by fitting the model to the field data¹.

The reduction of Fe-oxides is described by a similar rate equation:

$$-dC_{FeOOH}/dt = m_o \cdot 2.54 \cdot 10^{-11} \cdot (m_t/m_o)^{1.5} \cdot (1 - SR_{FeOOH}) \quad (mol/s)$$
(2)

The initial mass, m_o is 0.394 mol/L corresponding 65 µmol FeOOH/g obtained by extrapolation from the field data recalculated to the concentration per liter of contacting groundwater¹. m_t , the mass of FeOOH at time t and $2.45 \cdot 10^{-11}$ sec⁻¹ the rate constant determined by fitting the model to the field data¹. The exponent to (m_t/m_o) reflects the heterogeneity in the reactivity of the FeOOH and the value > 1 signifies that part of the FeOOH is less reactive. SR_{FeOOH} is the Saturation Ratio (IAP/K). In the model, the solubility of Fe-oxide (for the reaction FeOOH + 3H⁺ \rightarrow Fe³⁺ + 2H₂O) has a value of logK = 0.391 which is slightly more soluble than goethite and was found by fitting the model to field data. Accordingly the rate equation for FeOOH has a kinetic part, the first two terms, and a thermodynamic part, the last term. The thermodynamic part increases the rate at strong subsaturation and stops the rate when equilibrium is reached. The composition of the Fe-oxide was changed to contain 1.2 mmol As(V) per mol of Fe based on the analysis of sedimentary iron oxides by reductive dissolution at four different sites¹.

The treatment of As(III) sorption onto the sediment was changed from the original model formulation in Postma et al. $(2016)^1$ to be replaced by the adsorption isotherm measured by Nguyen et al. $(2014)^3$ on the Nam Du aquifer sediment from 5.5-6 m depth. In the input file it is formally given as a Langmuir isotherm but at the low As concentrations occurring in the Nam Du aquifer it is equivalent to a linear isotherm with K'_d of 12.6 L/kg

A major difference between the model application of Postma et al. $(2016)^1$ and the present one is that the transport rate in the former case was 0.5 m/yr while in the present case with bank infiltration it is 19 m/yr.

We use the WATEQ4F.DAT database² with the compilation of Langmuir et al. $(2006)^4$ for arsenic speciation. Both the input file and the database are available from the corresponding author.

PHREEQC-3 inputfile

```
# Model River water infiltration into the Nam Du aquifer
# The model is as Postma et al 2016 GCA, but with As(III) sorption from Nuygen
# et al 2014 GCA, added REACTION in cell 1 and no constant P_CO2
# database LangmuirAs_wateq4f.dat # wateq4f.dat with As species from Langmuir
# et al 2006 GCA v 70 2942-
SURFACE_MASTER_SPECIES
Langmuir Langmuir
SURFACE_SPECIES
Langmuir = Langmuir
Langmuir + H3AsO3 = LangmuirH3AsO3
-log_k 3.176 # Nguyen et al. (2014)GCA
-mole_balance LangmuirH3AsO3
PHASES
Fe(OH)3As
    Fe(OH)2.9964(AsO4)0.0012 + 2.9964H+ = Fe+3 + 2.9964H2O + 0.0012AsO4-3
           log_k
                       0.391 \quad #4.891-4.5 \text{ si} = -4.5,
# uses the measured sediment As/Fe 1.2 nM/uM Postma et al 2016
CCalcite
CaCO3 = Ca+2 + CO3-2
                       -8.23 #-8.48 + 0.25 = SI 0.25
           log_k
           delta_h -2.297 kcal
SSiderite
                                   #from PHREEOC.DAT
           FeCO3 = Fe+2 + CO3-2
           log k -9.89 #SI = 1. -10.89 + 1. = -9.89
           delta h -2.480 kcal
solution 0
               #river water
units mmol/L
рН 8.3
         #river has 8.3
O(0) 0.48
temp 28.8
Na
    0.2
K 0.05
Ca 0.66
Mg 0.23
Si 0.16
F 8.79 umol/L
Cl 89.48 umol/L
N(+5) 23.29 umol/L
Alkalinity 1.7 meq/L
solution 1-40
                # taken from H-transect as average at elevation -5m
units mmol/L
temp 27
рН 7.0
Alkalinity 10. meg/L
As(3) 1. umol/L # before 4
```

```
Fe(2) 0.3
C(-4) 1.0
Ca 3
Mg 2
Na 0.25
к 0.1
Cl 0.1
#Here adsorption is disabled to produce Fig.3 results.
#To generate Fig.4 with sorption, enable the next 4 lines
#SURFACE 3-40 #Nguyen etal 2014 GCA with por.0.36 At low As ~ to K'= 12.6 L/kg
#Langmuir 3.96E-02 1 1 # 4711 g/L *8.4e-6 mol site /g = 3.96E-02 mol site
#-no edl
#-equilibrate 1
RATES
CCalcite
           -start
5
           if (m \le 0.0) then goto 210
7
           sr CC = sr("CCalcite")
10
           if (sr_CC \ge 1.0) then goto 210
40
           moles = m0*(7.5e-4/3.15e7) * (m/m0)^3.0 * time * (1-sr_CC)
           if moles > m then moles = m
70
210
           save moles
           -end
SSiderite
           -start
7
           sr_SS = sr("SSiderite")
40
           moles = (1e-4/3.15e7) * time * (1-sr_SS)
210
           save moles
           -end
Fe(OH)3As
           -start
5
           if (m \le 0.0) then goto 210
7
           sr_fe = sr("Fe(OH)3As")
10
           if (sr_fe \ge 1.0) then goto 210
           moles = m0*(0.8e-3/3.15e7) * (m/m0)^1.5 * time * (1-sr_fe)
40
70
           if moles > m then moles = m
210
           save moles
           -end
Organic
     -start
5
           if (m \le 0.0) then goto 20
      moles = m0*(2.94e-4/3.15e7) * (m/m0)^2.5
10
           if moles > m then moles = m
11
20
      save moles * time
     -end
KINETICS 2
CCalcite
-m0 10.
KINETICS 3-40
SSiderite
-m0 0.0
Organic
 -formula C
 -m0 1.36 # 0.27% org C
Fe(OH)3As
-m0 0.394
```

```
-bad_step_max 4000
-cvode true
REACTION 2 # to simulate DOC consumption in top layer
С
   1.0
0.27e-3 moles
                  # 1000*0.27e-3*365/19.2 = 5.1 mM/yr
TRANSPORT
-cells 40
-shifts 1900 # 1 year = 365 d/19.2 d = 19.01 shift,
-time step 1.66e6 # 19 m/yr. 1m = 0.053 yr = 0.053 *3.15e7 sec = 1.66e6 sec (=
19.2 days)
-lengths 1.
-punch frequency 190
SELECTED OUTPUT
-file M:\dieke\PHRQout.xls # adjust
-totals
          Ca N(5) Fe(2) C(-4) S(6) S(-2) Br As(5) As(3)
-alkalinity
-saturation_indices
                     CO2(g) siderite calcite Fe(OH)3As
-equilibrium phases Siderite calcite FeS(ppt)
-molalities 02 LangmuirH3AsO3 Langmuir H3AsO3
-kinetic reactants Organic Fe(OH)3As CCalcite SSiderite
PRINT
-reset
         false
end
```

REFERENCES

(1) Postma, D; Pham, T. K. T.; Sø, H. U.; Hoang, V. H.; Vi, M. L.; Nguyen, T. T.; Larsen, F.; Pham, H. V.; Jakobsen, R. A model for the evolution in water chemistry of an arsenic contaminated aquifer over the last 6000 years, Red River floodplain, Vietnam. *Geochim. Cosmochim. Acta* **2016**, *195*, 277–292.

(2) Parkhurst, D. L.; Appelo, C. A. J. Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: *U.S. Geological Survey Techniques and Methods*, **2013**, book 6, chap. A43, 497 p., available only at <u>http://pubs.usgs.gov/tm/06/a43</u>

(3) Nguyen, T. H. M.; Postma, D.; Pham, T. K. T.; Jessen, S.; Pham, H. V.; Larsen, F.; Adsorption and desorption of arsenic to aquifer sediment on the Red River floodplain at Nam Du, Vietnam. *Geochim. Cosmochim. Acta* **2014**,*142*, 587-600.

(4) Langmuir, D. L.; Mahoney, J.; Rowson J. Solubility products of amorphous ferric arsenate and crystalline scorodite (FeAsO₄·2H₂O) and their application to arsenic behavior in buried mine tailings. *Geochim. Cosmochim. Acta* **2006**, *70*, 2942-2956.