Reactive Transport Modeling:

Arsenic in the Red River Floodplain, Vietnam

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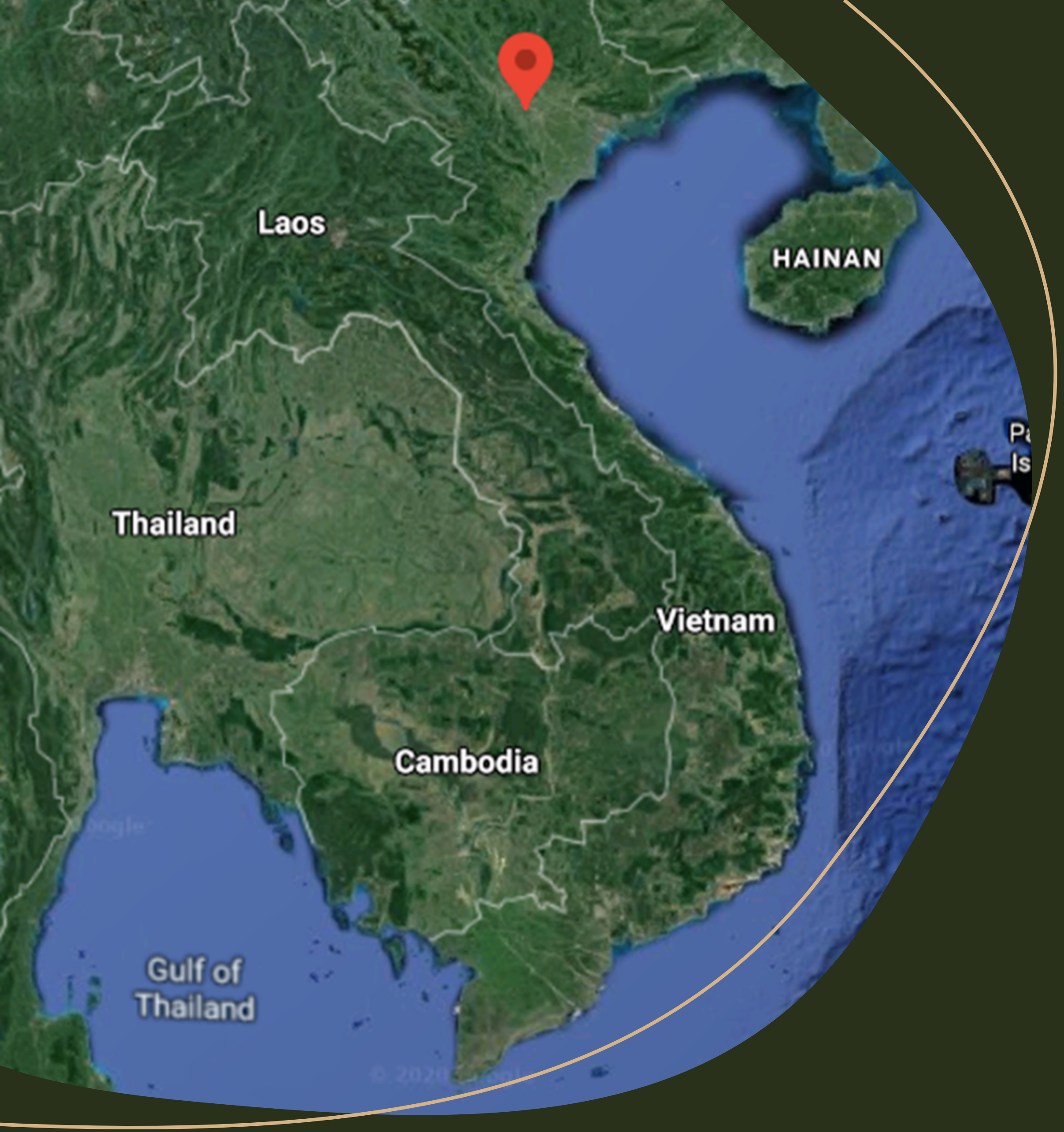
Red River Floodplain

- Major Population Centers
  - Hanoi, Vietnam
- Up to 11 million people at risk of arsenic exposure (Postma et al. 2007)
- WHO drinking water limit 10 μg/L

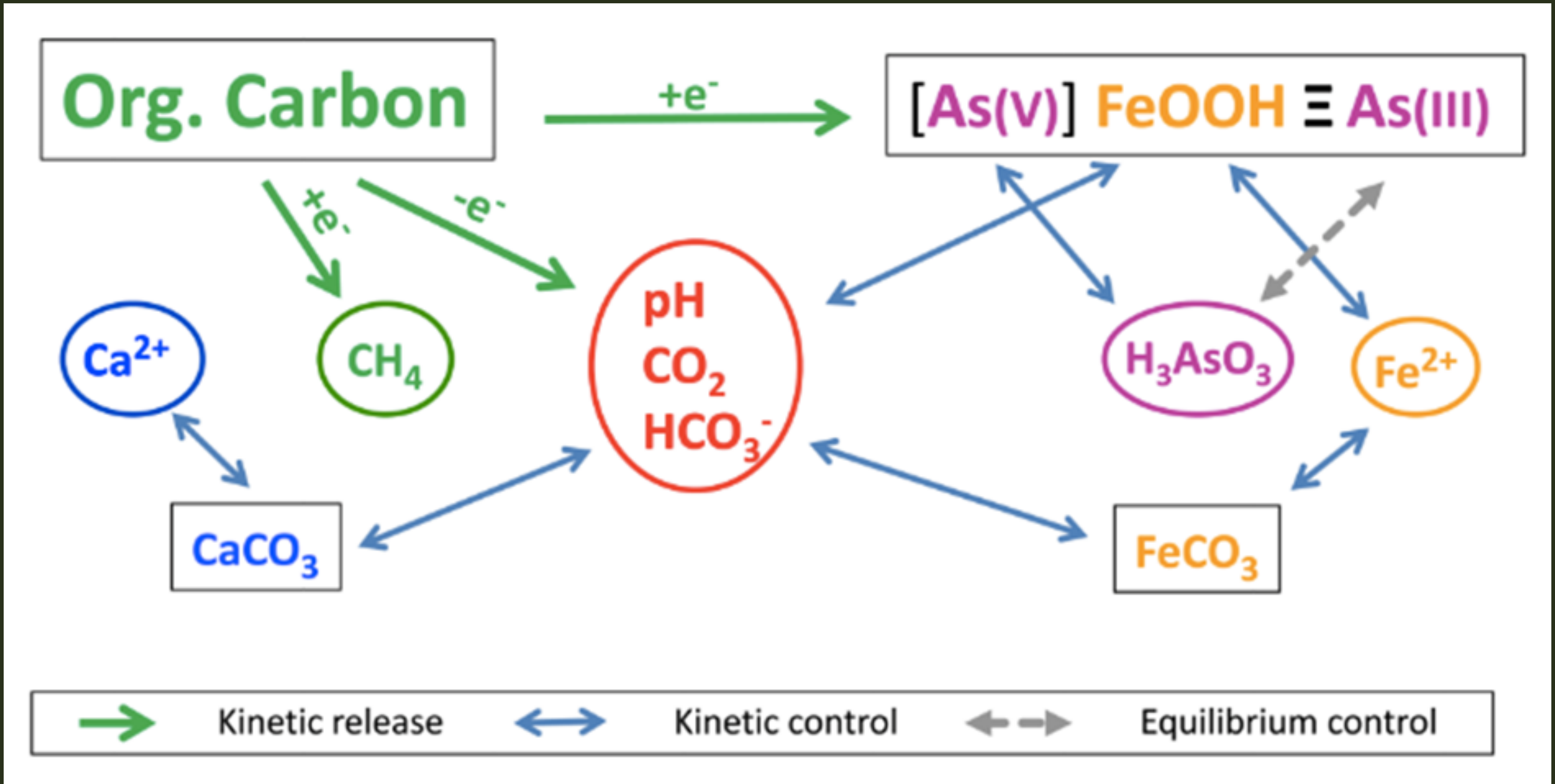
Red River Floodplain Aquifers

- Holocene Aquifers
  - Deposited 500 – 6000 yrs ago
- Sandy fluvial channel and sand bar deposits overlain by clay overbank deposits
- Recharged through outcropped sand or fractured clay
- Anoxic aquifer conditions



Past research

- Complicated hydrological conditions
  - Channel modification
  - Agriculture
- Three arsenic mobilization theories
  - Fe-oxide reduction
  - Sediment desorption within aquifer
  - Mobilization at surface

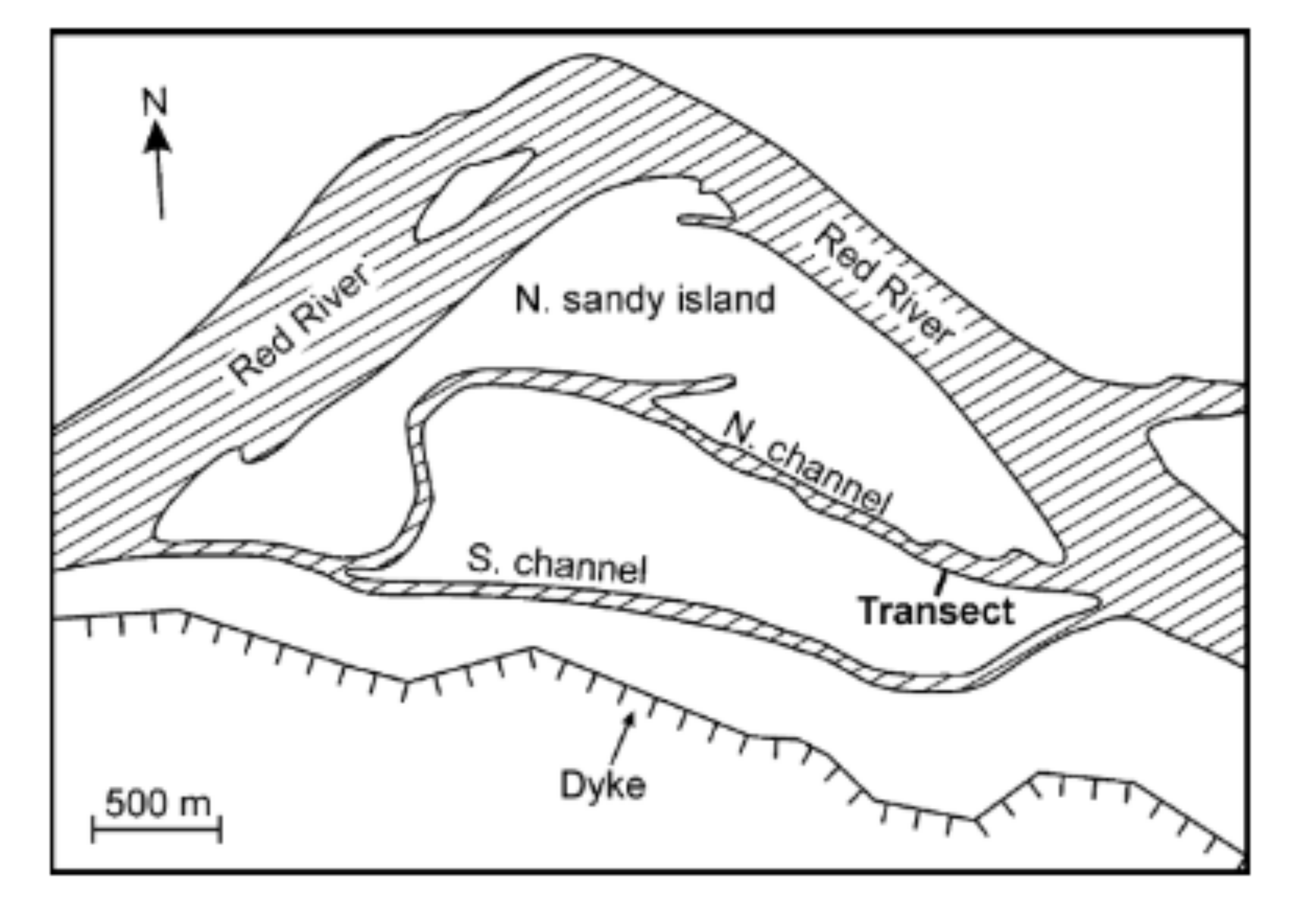


Postma et al. 2016

Schematic of Key Processes

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

Postma et al. 2007



Postma et al. 2007

Goals:

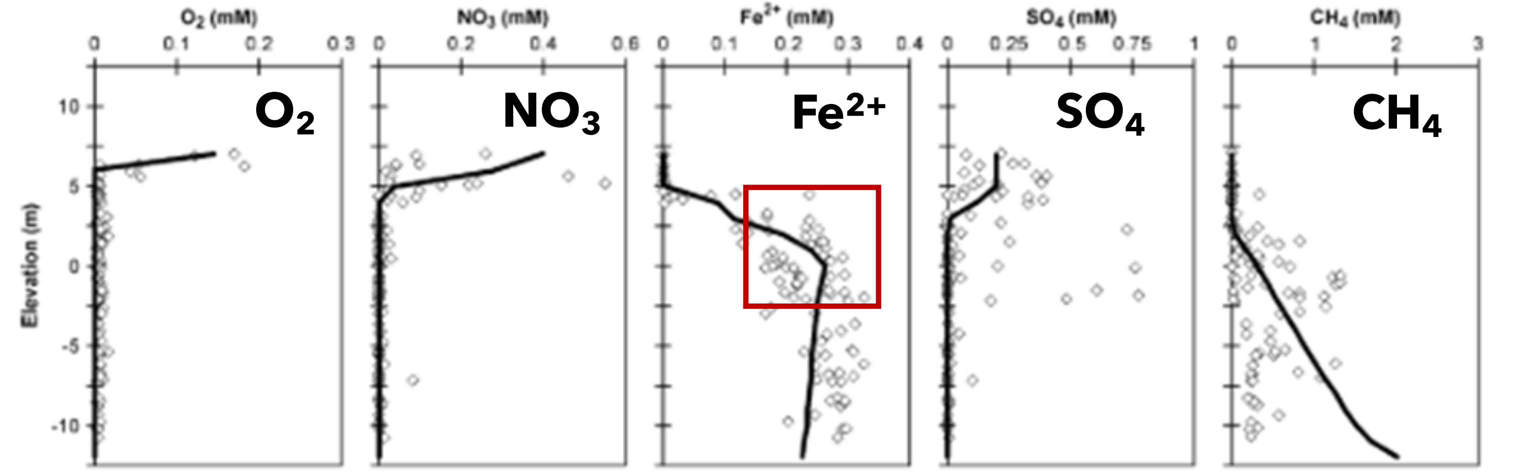
- Analysis of groundwater chemistry
- PHREEQC transport modeling
  - Arsenic mobilization and transportation
  - Fit model to field observation

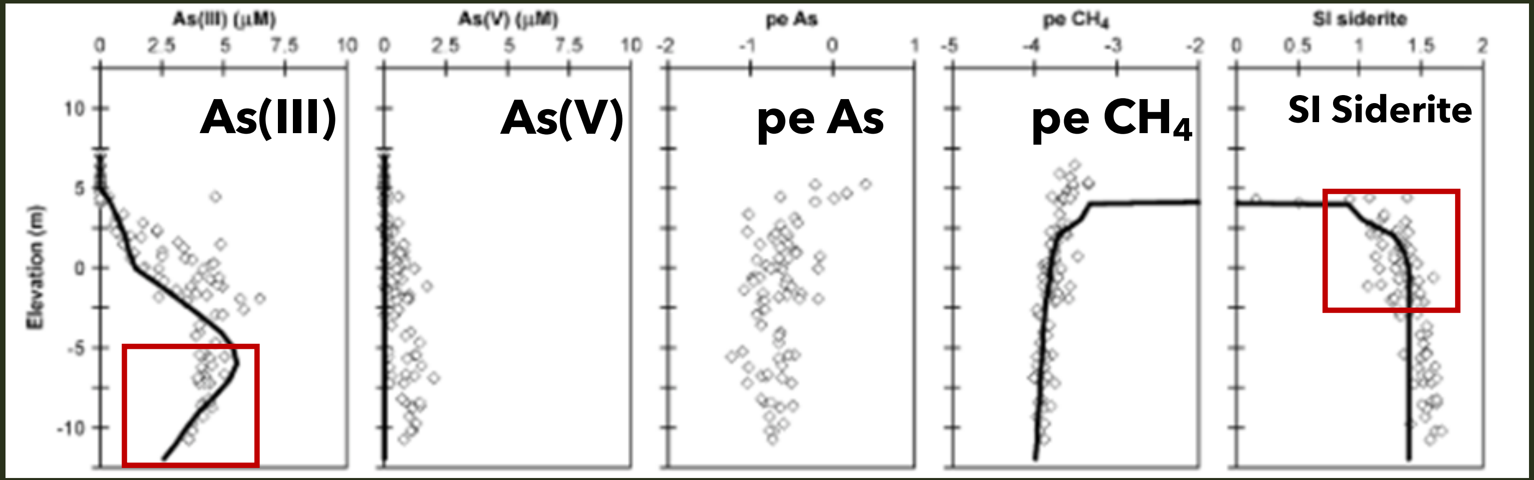
Table 2
Water composition in the Red River and in the groundwater of borehole H51 at elevation 0.3 m (Fig. 2)

	River water	Ground water
EC (μS/cm)	290	880
Temp. (°C)	30	26.4
O_2 (mmol/L)	0.3	0
pH	7.18	6.95
As total (μmol/L)	<0.01	5.4
As(III) (μmol/L)	—	4.6
Fe(2+) (mmol/L)	<0.001	0.27
Mn (mmol/L)	<0.0009	0.001
Ca (mmol/L)	0.53	2.76
Mg (mmol/L)	0.18	1.91
Na (mmol/L)	0.2	0.23
K (mmol/L)	0.04	0.1
NH_4 (mmol/L)	<0.006	0.17
Alkalinity (meq/L)	2.38	10.2
SO_4 (mmol/L)	0.06	0
Cl (mmol/L)	0.11	0.08
NO_3 (mmol/L)	0.01	0
PO_4 (mmol/L)	<0.001	0.010
Si (mmol/L)	0.27	0.57
CH_4 (mmol/L)	—	0.57
SI calcite	−0.64	0.26
$\log P_{CO_2}$	−1.98	−1.18

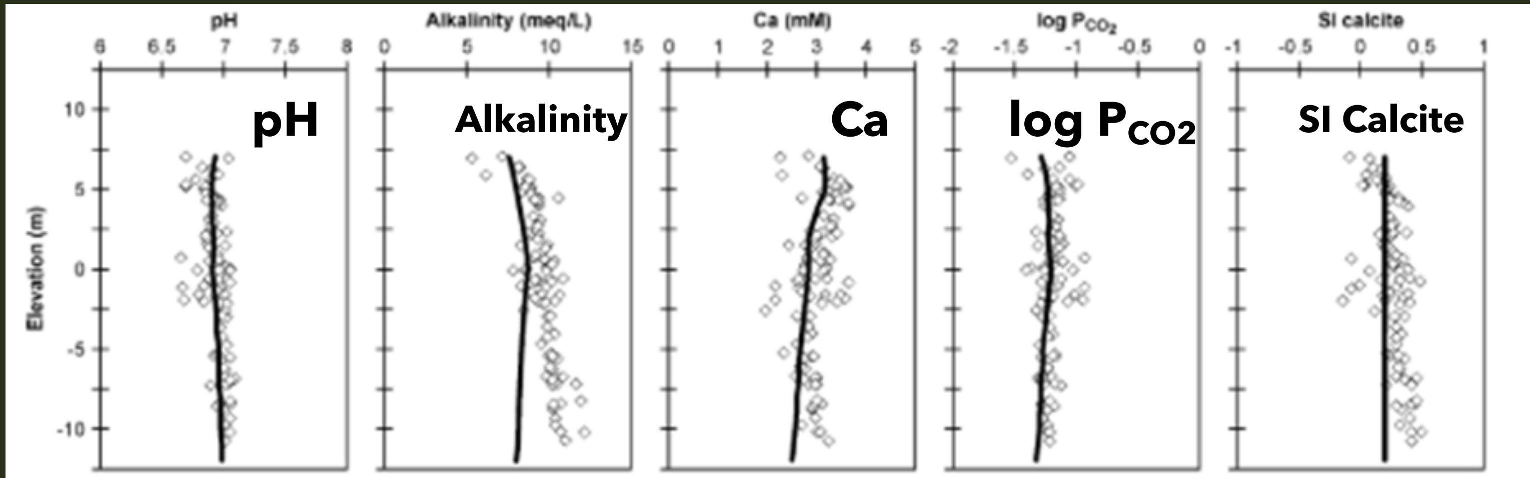
Geochemical Analysis

Postma et al. 2007





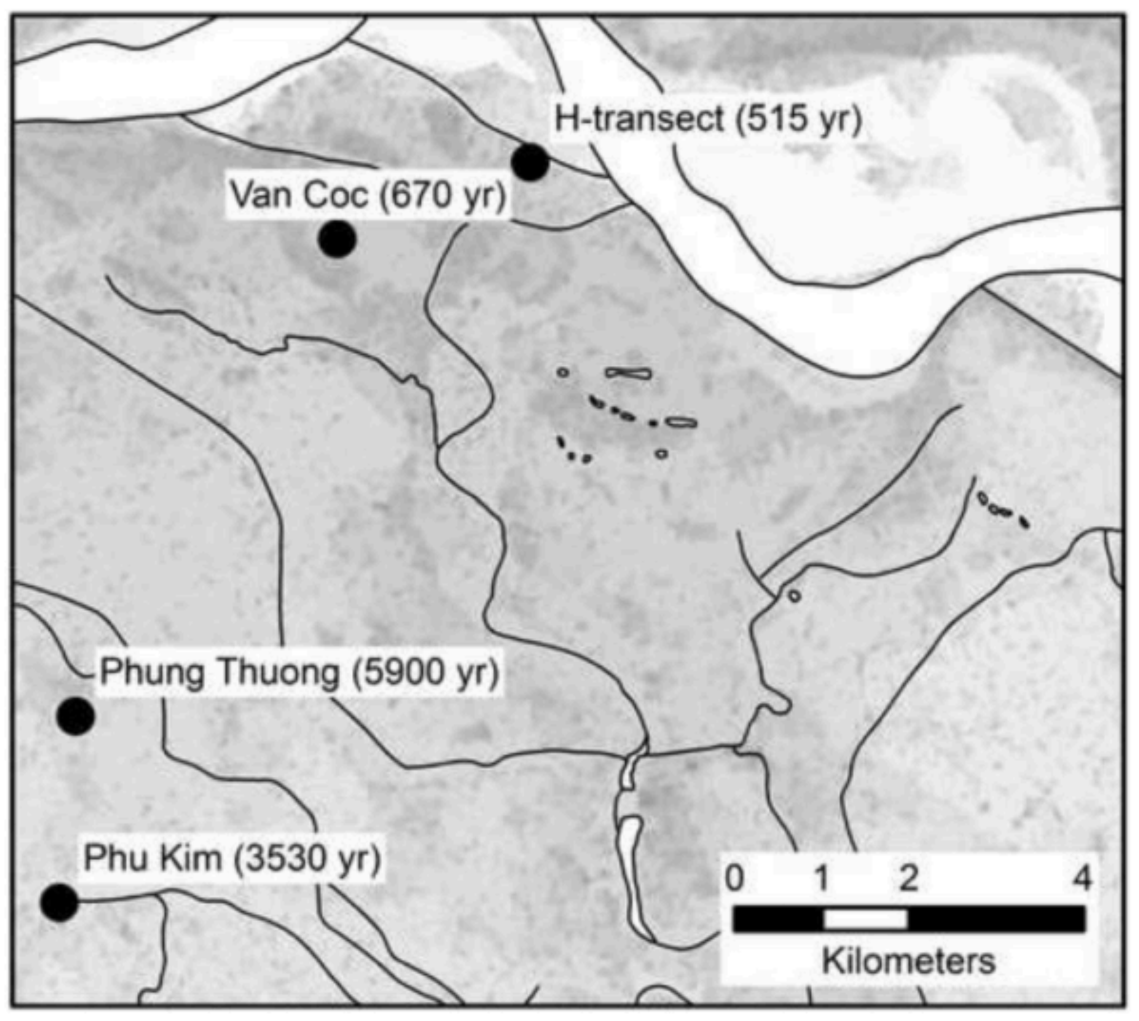
Reactive Transport Results



Postma et al. 2007

A model for the evolution in water chemistry of an arsenic contaminated aquifer over the last 6000 years, Red River floodplain, Vietnam

Postma et al. 2016



Goals:

- Model full range of depositional ages
- Improve model with kinetic reactions

Postma et al. 2016

PHREEQC Input

- Surface Master Species
  - Langmuir Arsenic Speciation
- Surface Species
  - Speciation Reactions
- Phases
  - Define Kinetic Reactions

```
#database LangmuirAs_wateq4f.dat

SURFACE_MASTER_SPECIES
Langmuir Langmuir

SURFACE_SPECIES
Langmuir = Langmuir
Langmuir + H3AsO3 = LangmuirH3AsO3
-log_k 3.176
-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
# uses the measured sed As/Fe 1.2 nM/uM

CCalcite
CaCO3 = Ca+2 + CO3-2
      log_k  -8.23
      delta_h -2.297 kcal

SSiderite                                  #from PHREEQC.DAT
      FeCO3 = Fe+2 + CO3-2
      log_k -9.89  #SI = 1.  -10.89 + 1. = -9.89
      delta_h  -2.480 kcal
```

Postma et al. 2016

PHREEQC Input

- Solution Composition
  - Infiltrating
  - Initial Groundwater
- Surface
  - Surface Site Density
- Equilibrium Phases
  - Equilibrate with CO_2

```
solution 0   #Red River water  (Postma et al. 2007, GCA v71.5054-)
temp  27
units  mmol/l
pH    7.18
O(0)  0.4
Ca    0.53
Mg   1
Na 0.2
K 0.04
Alkalinity 2.38
#S(6) 0.06
Cl 0.11
#N(5) 0.01
Si 0.27

SOLUTION  1-40
temp 27
units  mmol/l
pH    7.18
As 1e-10
Ca    0.53
Mg   0.18
Na 0.2
K 0.04
Alkalinity 2.38
Cl 0.11
Si 0.27
```

```
SURFACE 2-40
Langmuir Fe(OH)3As kin 0.07 8.9e3
-no_edl
-equilibrate 1
```

```
EQUILIBRIUM_PHASES 1
CO2(g) -1.1 30
```

Postma et al. 2016

PHREEQC Input

- Rates of Kinetic Reactions
  - $-\frac{dC_{CaCO_3}}{dt} = m_o * 2.38 * 10^{-11} * \frac{m_t}{m_o}^{3.0} * (1 - SR_{CaCO_3})$
  - $-\frac{dC_{FeCO_3}}{dt} = 3.17 * 10^{-12} * \left(1 - SR_{FeCO_3}\right)$
  - $-\frac{dC_{FeOOH}}{dt} = m_o * 2.54 * 10^{-11} * \frac{m_t}{m_o}^{1.5} * (1 - SR_{FeOOH})$
  - $-\frac{dC_c}{dt} = m_o * 9.3 * 10^{-12} * \frac{m_t}{m_o}^{2.5}$

```
RATES
CCalcite
        -start
5       if (m <= 0.0) then goto 210
7       sr_CC = sr("CCalcite")
10      if (sr_CC >= 1.0) then goto 210
40      moles =  m0*(7.5e-4/3.15e7) * (m/m0)^3.0 * time * (1-sr_CC)
70      if moles > m then moles = m
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 <= 0.0) then goto 210
7       sr_fe = sr("Fe(OH)3As")
10      if (sr_fe >= 1.0) then goto 210
40      moles =  m0*(0.8e-3/3.15e7) * (m/m0)^1.5 * time * (1-sr_fe)
70      if moles > m then moles = m
210     save moles
        -end
Organic
                   -start
5       if (m <= 0.0) then goto 20
10                 moles = m0*(2.94e-4/3.15e7) * (m/m0)^2.5
11      if moles > m then moles = m
20                 save moles * time
                 -end
```

Postma et al. 2016

PHREEQC Input

- Kinetics
  - Cell 1
    - Calcite Dissolution
  - Cell 2-40
    - Siderite Precipitation
    - Organic Carbon Degradation
    - Fe-Oxide Reduction
- Transport
  - 6000 Years
  - 20 Meter Vertical Column
- Selected Output

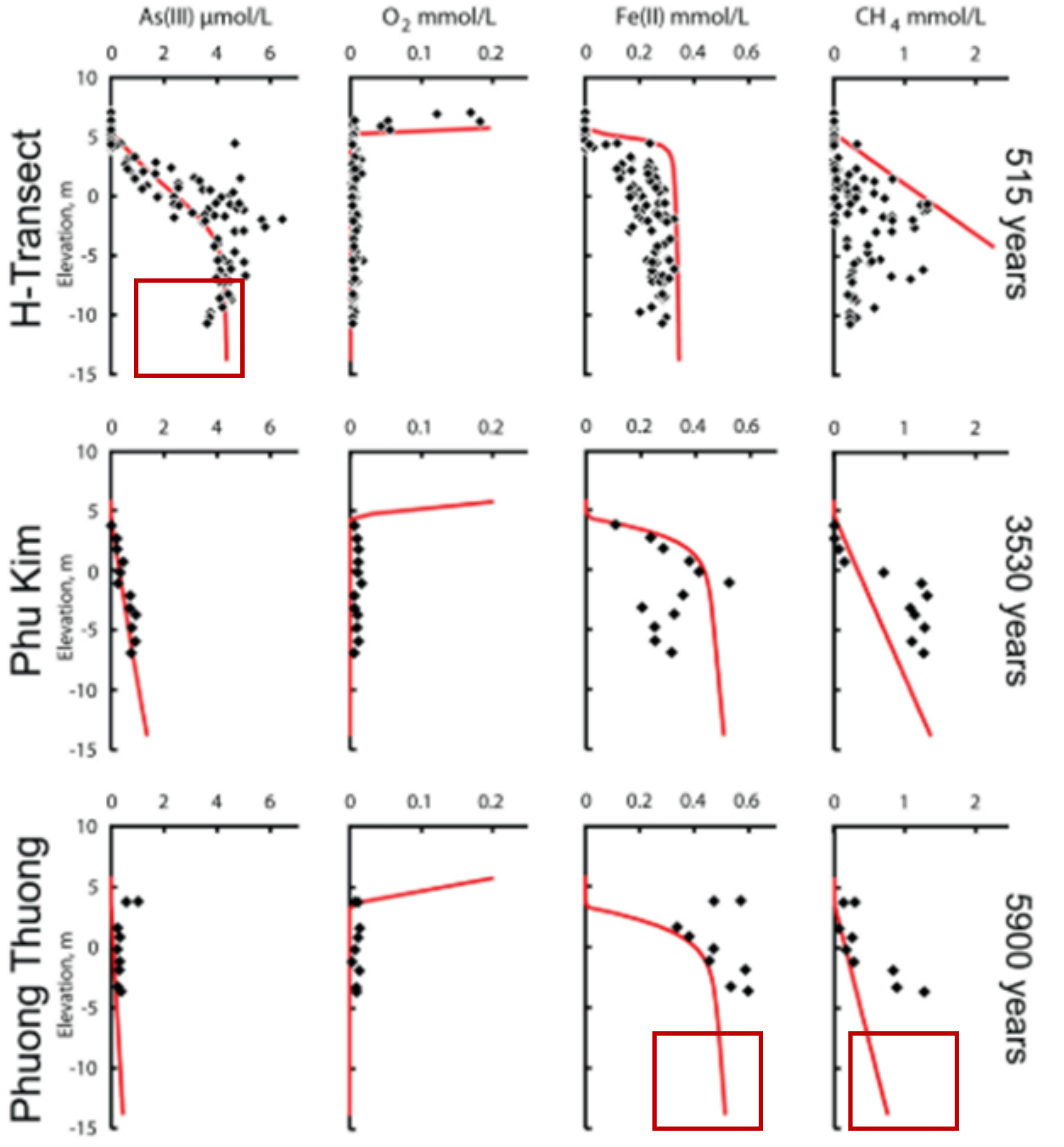
```
KINETICS 1
CCalcite
-m0 10.

KINETICS 2-40
SSiderite
-m0 0.0
Organic
 -formula C
 -m0 1.36   # 0.27% org C
Fe(OH)3As
-m0 0.394 #65 umol/g
-bad_step_max 4000
-cvode true
```

```
TRANSPORT
    -cells                      40
    -shifts                     6000
    -time_step                  31536000 # seconds = 1 year
    -lengths                    40*0.5
    -print_frequency            200
    -punch_frequency            200
```

```
SELECTED_OUTPUT
-file C:\Users\jorda\Desktop\Geochem\Postma_2016_mod2.sel
-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 O2 LangmuirH3AsO3 Langmuir H3AsO3
-kinetic_reactants Organic Fe(OH)3As CCalcite SSiderite
```

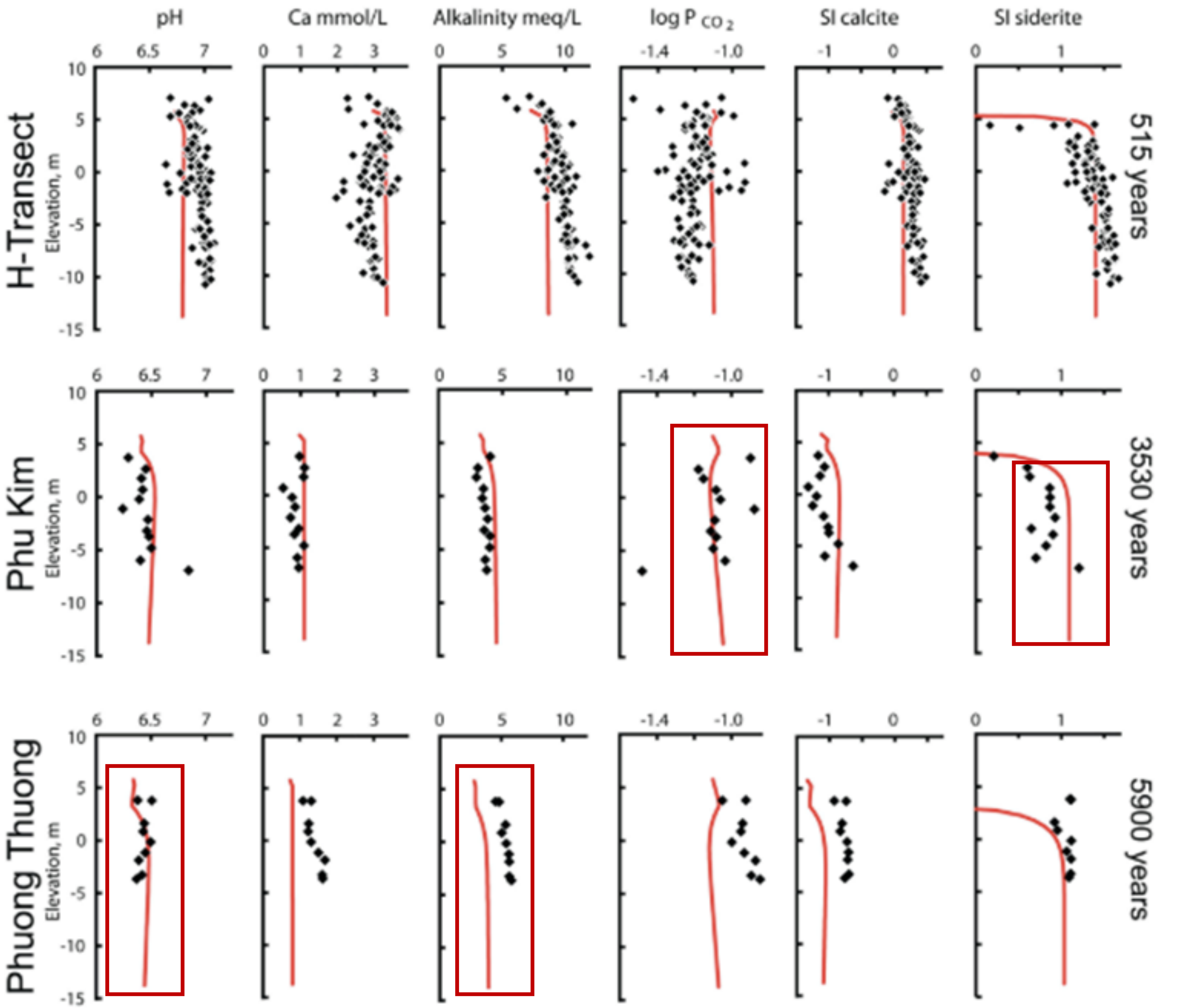
Postma et al. 2016

Postma et al. 2016 Results



Postma et al. 2016

- After 1000 years
  - Reduction in As(III)
  - More aqueous Fe(II)
  - Less CH_4 Production
  - Lower pH
  - Lower Alkalinity
  - Less stable P_{CO2}
  - Siderite Dissolves

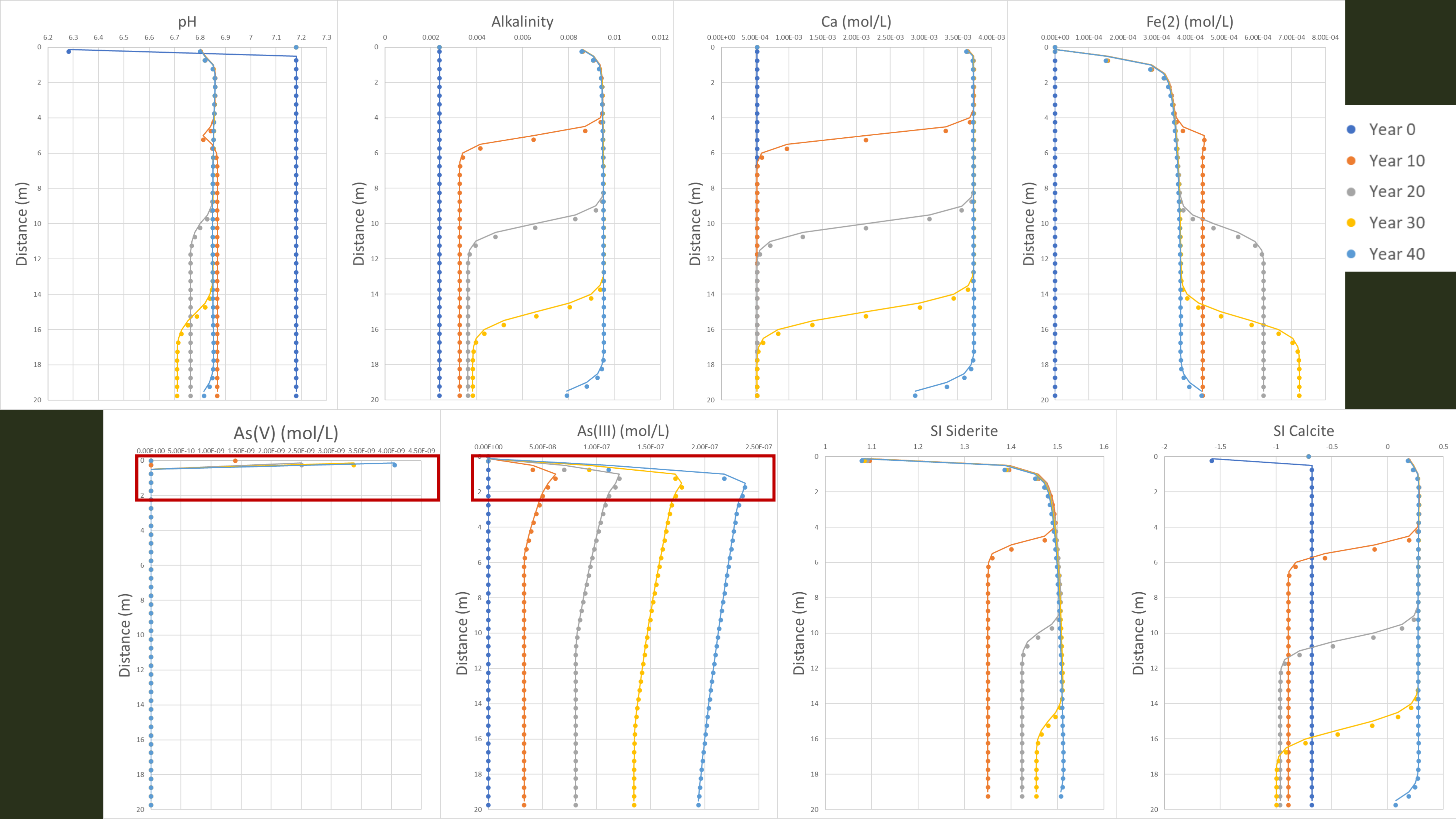


Postma et al. 2016

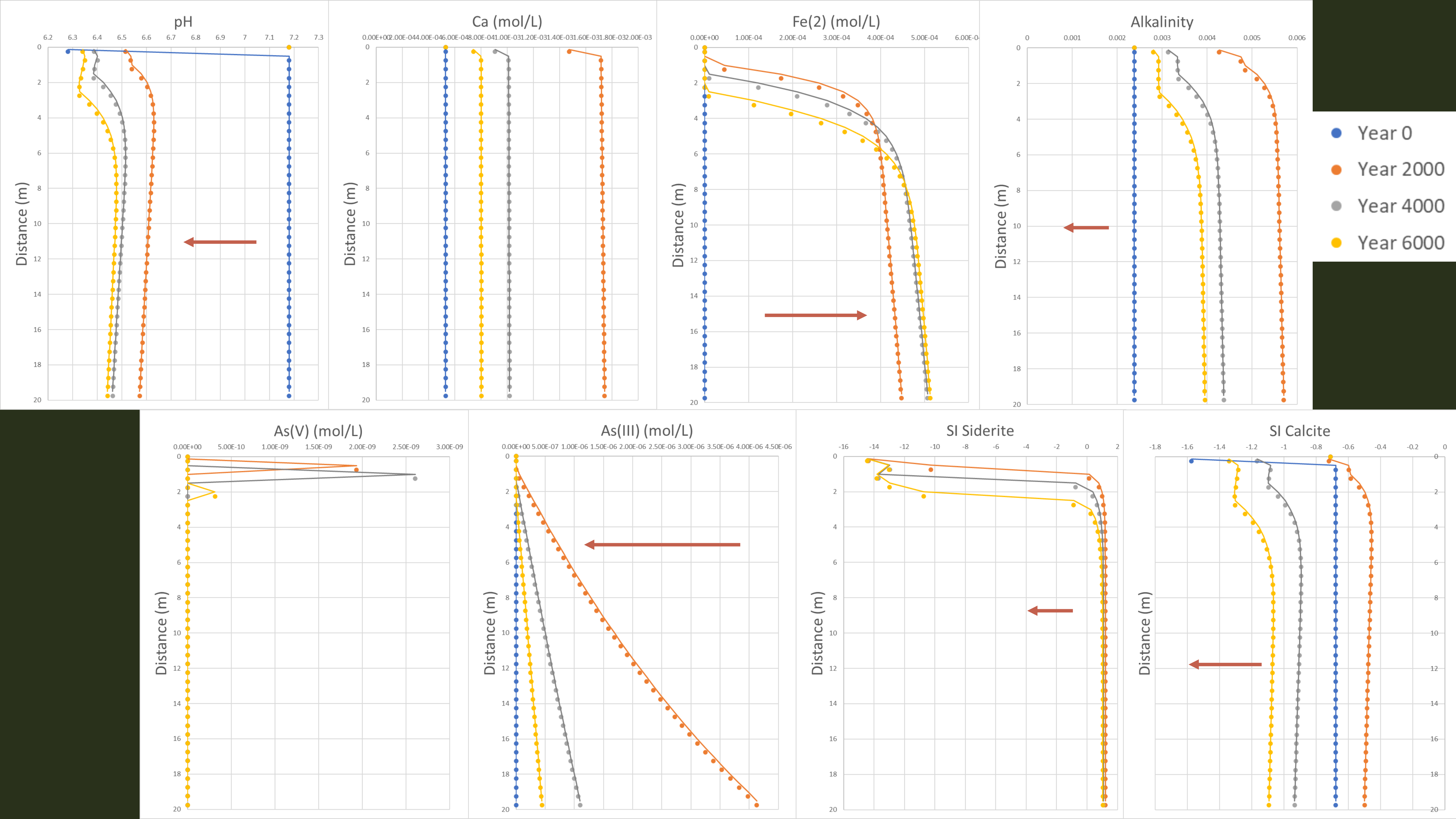
PHREEQC Input Modification

- Transport
  - 40 Cells
    - 0.5 Meters long
    - 20 Meter Vertical Column
  - 40 Shifts
    - 40 years
  - Print Every 5 Shifts

```
TRANSPORT
    -cells                      40
    -shifts                     40
    -time_step                  31536000 # seconds = 1 year
    -lengths                    40*0.5
    -print_frequency            5
    -punch_frequency            5
```



pH
Alkalinity
Ca (mol/L)
Fe(2) (mol/L)
As(V) (mol/L)
As(III) (mol/L)
SI Siderite
SI Calcite
Distance (m)
Year 0
Year 10
Year 20
Year 30
Year 40


pH
Ca (mol/L)
Fe(2) (mol/L)
Alkalinity
Year 0
Year 2000
Year 4000
Year 6000
As(V) (mol/L)
As(III) (mol/L)
SI Siderite
SI Calcite
Distance (m)

Conclusions

1. Kinetic reaction rates allow for more accurate longer-term modeling

2. Organic carbon reactivity is limiting agent, and is inversely related to time

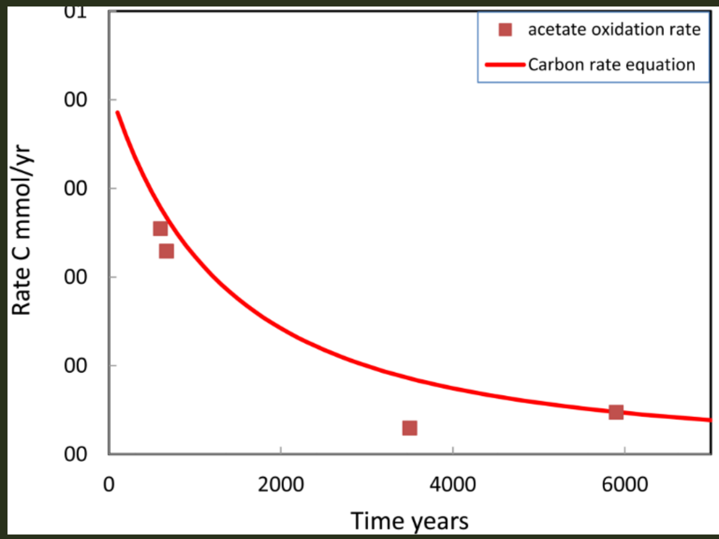
3. Dynamic stability over the first ~1000 years

    1. $7CH_2O + 4FeOOH \rightleftharpoons 4FeCO_3 + 3CH_4 + 3H_2O$

4. As(III) concentration peaks at ~ 1200 years

    1. 600 µg/L - 60 times the WHO drinking water limit

    2. At 6000 years concentrations are still more than 3 times the WHO limit



Postma et al. 2016

References

- Parkhurst, D. L., & Appelo, C. a. J. (2013). 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, book 6, chapter A43, 497 p. *U.S. Geological Survey Techniques and Methods, Book 6, Chapter A43*, 6-43A.
- 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. (2016). A model for the evolution in water chemistry of an arsenic contaminated aquifer over the last 6000 years, Red River floodplain, Vietnam. *Geochimica et Cosmochimica Acta*, *195*, 277–292. https://doi.org/10.1016/j.gca.2016.09.014
- Postma, D., Larsen, F., Minh Hue, N. T., 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. *Geochimica et Cosmochimica Acta*, *71*(21), 5054–5071. https://doi.org/10.1016/j.gca.2007.08.020
- Thi Hoa Mai, N., Postma, D., Thi Kim Trang, P., Jessen, S., Hung Viet, P., & Larsen, F. (2014). Adsorption and desorption of arsenic to aquifer sediment on the Red River floodplain at Nam Du, Vietnam. *Geochimica et Cosmochimica Acta*, *142*, 587–600. https://doi.org/10.1016/j.gca.2014.07.014