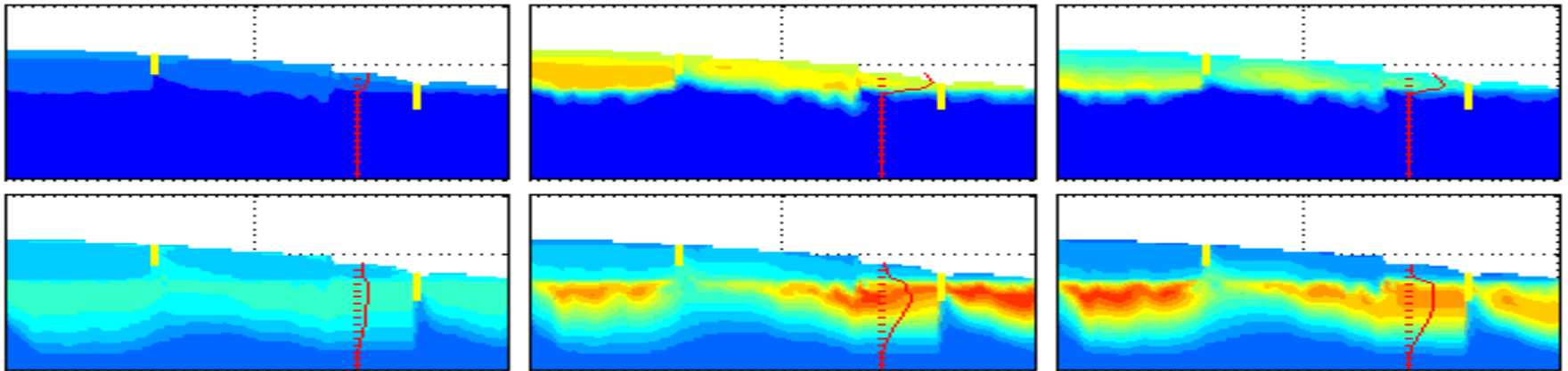




Process-based modelling of arsenic fate and remediation: From the lab- towards the field-scale



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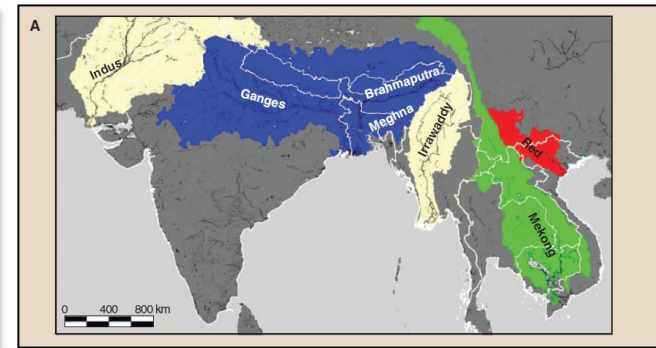
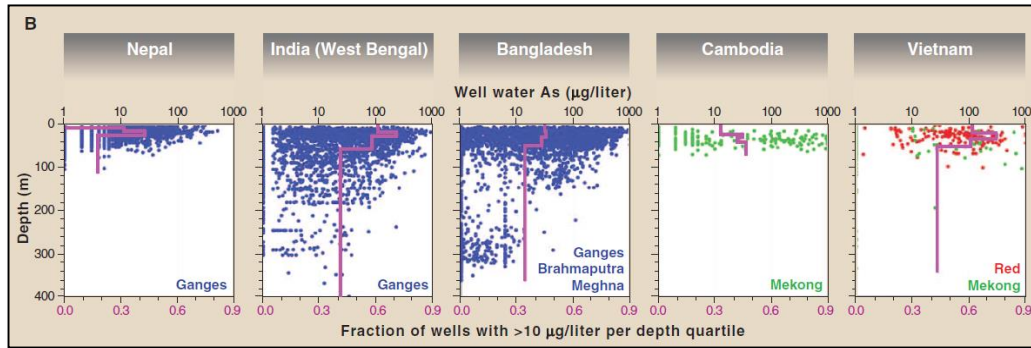


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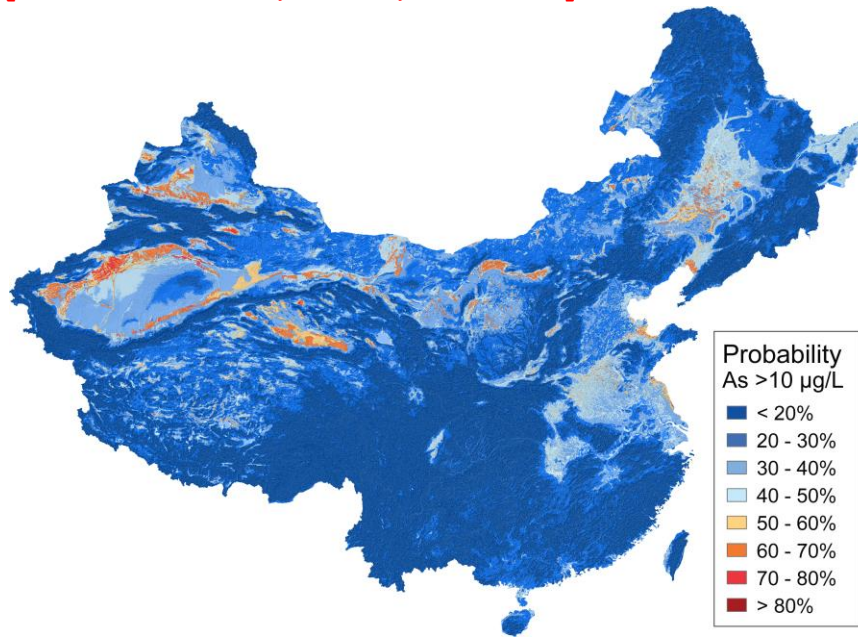
Outline

- Background
- Modelling the fate of arsenic across spatial scales – development and testing of conceptual and numerical models
 - Arsenic release from ferrihydrite-coated sand columns
 - Field-scale sucrose injection experiment (Bengal)
 - Arsenic release and migration Van Phuc (Vietnam)
 - In situ As remediation via in situ magnetite formation
- Concluding Remarks

Background



[Fendorf et al., 2010, *Science*]



[Rodriguez-Lado et al., 2013, *Science*]

- As groundwater contamination is widespread in many parts of Asia, especially the big river deltas
- $\geq 100\text{M}$ people affected
- As mostly prevails in the more shallow wells (Holocene)
- Deep wells show little or no As (Pleistocene)

Background

What can geochemists and hydrogeologists contribute to minimise As exposure ?


- Develop understanding of which geochemical and which hydrogeological factors can explain the heterogeneous distribution of As-affected wells

What can reactive transport modelling contribute ?

- Model-based analysis of data
 - Develop process-based quantitative tools that allow to analyze lab- and field-scale observations
 - Identify the controlling physical and geochemical processes and how they interact
- Predictive modeling:
 - Predict how long low-As wells will remain safe – depending on the implemented water management strategies
 - Assist the development of in situ As remediation techniques

Background

Process-based reactive transport modeling

- Integration of different data types (geological, geochemical, ...) through coupling flow/solute transport models with geochemical models
 - Bridge understanding/expertise of geochemists and hydrogeologists
 - Refine and evaluate conceptual model(s), ideally using 'high-quality' data sets that provide sufficient constraints to develop process-based models
 - Approach: From well constrained lab-scale towards field-scale
 - Lab Experiments
 - Controlled small-scale field experiments
 - Highly instrumented field site
- 
- well-controlled
- more representative



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Jim Davis, Lawrence Berkeley National Laboratory
Scott Fendorf, Stanford University

Impact of iron transformations on arsenic mobility in a
lactate-amended column system

Development and Testing of Model Approaches: Reductive Dissolution of Ferrihydrite

- Small-scale (5cm) column experiments
- Arsenic mobilization by reductive dissolution of iron oxides [Tufano and Fendorf, 2008, ES&T]
- 4 columns, each containing

9.5 g ferrihydrite-coated sand

44 mg ferrihydrite

3.19 mg arsenite

- Varying influent concentrations of organic carbon

(i) no lactate (control)



(ii) 0.08 mM lactate



(iii) 0.8 mM lactate



(iv) 7.7 mM lactate



Environ. Sci. Technol.

Confounding Impacts of Iron Reduction on Arsenic Retention

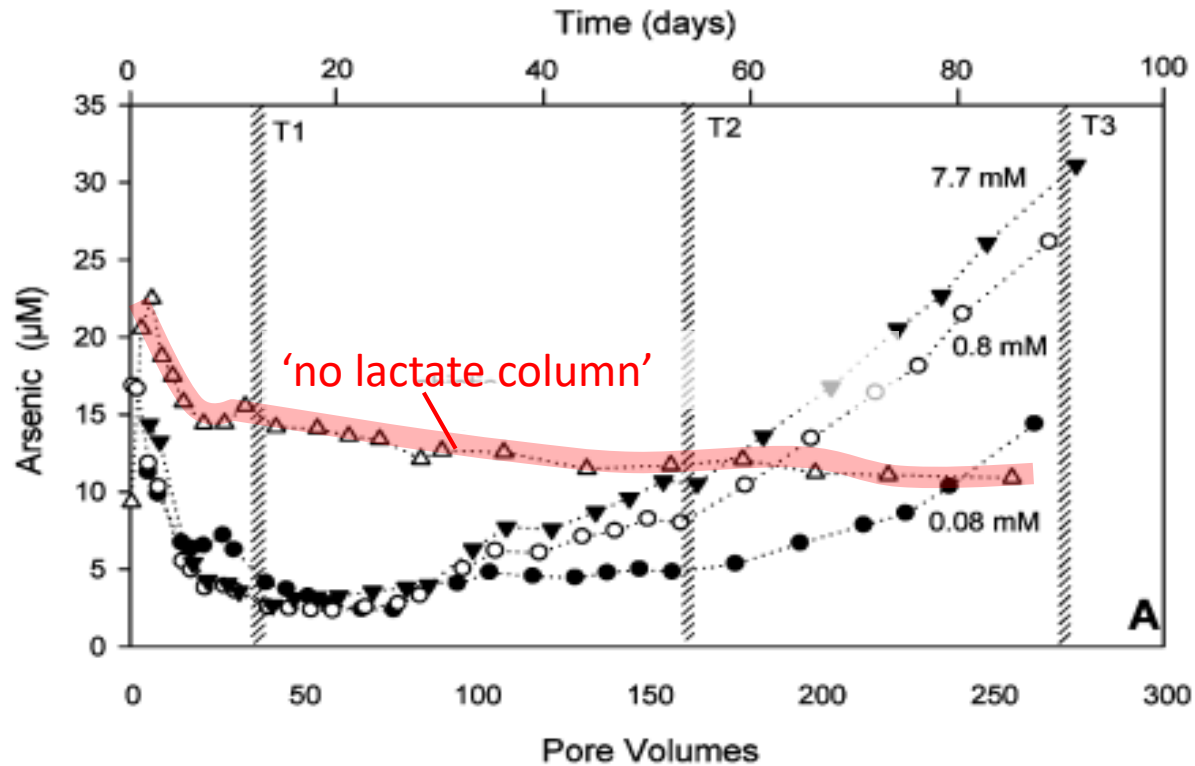
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March 17, 2008. Accepted March 18, 2008.

A transition from oxidizing to reducing conditions has long been implicated to increase aqueous As concentrations, for which reductive dissolution of iron (hydr)oxides is commonly implicated as the primary culprit. Confounding our understanding of processes controlling As retention, however, is that reductive transformation of ferrihydrite has recently been shown to promote As retention rather than release. To resolve the role iron phases have in regulating arsenic concentrations, here we examine As desorption from ferrihydrite-coated sands presorbed with As(III); experiments were performed at circumneutral pH under Fe-reducing conditions with the dissimilatory iron reducing bacterium *Shewanella putrefaciens* strain CN-32 over extended time periods. We reveal that with the initial phase of iron reduction, ferrihydrite undergoes transformation to secondary phases and increases As(III) retention (relative to abiotic controls). However, with increased reaction time, cessation of the phase transitions and ensuing reductive dissolution result in prolonged release of As(III) to the aqueous phase. Our results suggest that As(III) retention during iron reduction is temporally dependent on secondary precipitation of iron phases; during transformation to secondary phases, particularly magnetite, As(III) retention is enhanced even relative to oxidized systems. However, conditions that retard secondary transformation (more stable iron oxides or limited iron reducing bacterial activity), or prolonged anaerobiosis, will lead to both the dissolution of ferric (hydr)oxides and release of As(III) to the aqueous phase.

Experimental Results



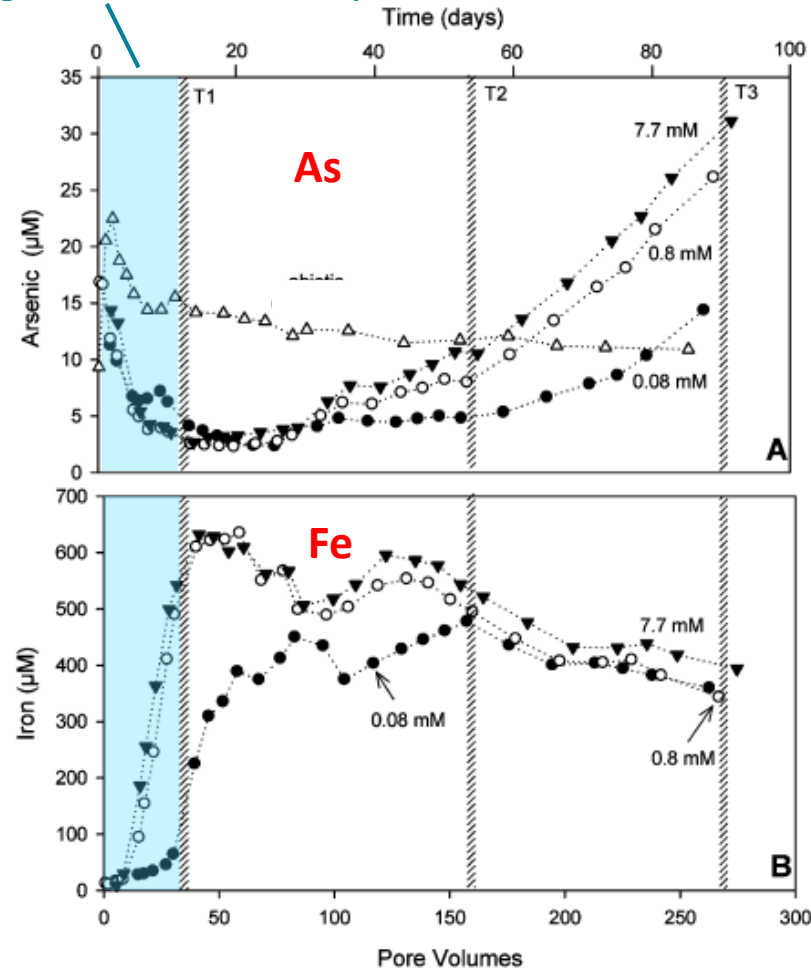
[Tufano and Fendorf, 2008, *ES&T*]

- Effluent As concentration initially **highest in control column** !!!???

Original Conceptual Model (Tufano and Fendorf)

- Lactate induces continuous reduction of ferrihydrite
- Sorbed As(III) is released from ferrihydrite as sorption sites are destroyed
- Ferrihydrite is partially transformed to magnetite
- Sorption to magnetite causes effluent As(III) concentrations to be lower in lactate-amended columns
- Decrease of As(III) effluent concentration caused by sorption to freshly formed magnetite

Magnetite formation phase

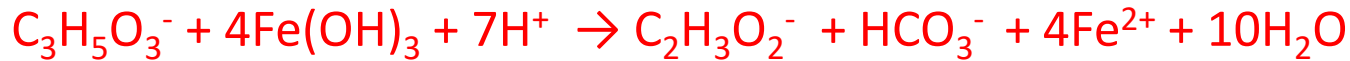


[Tufano and Fendorf, 2008, ES&T]

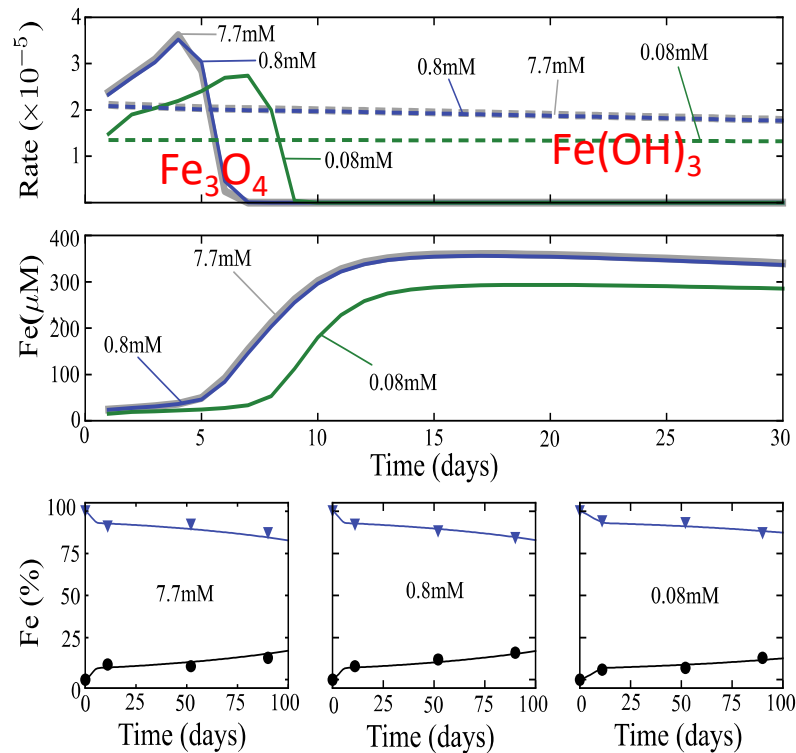
Modeling Ferrihydrite Reduction and Magnetite Formation

Key Elements of Reaction Network

- Lactate oxidation + Ferrihydrite reduction

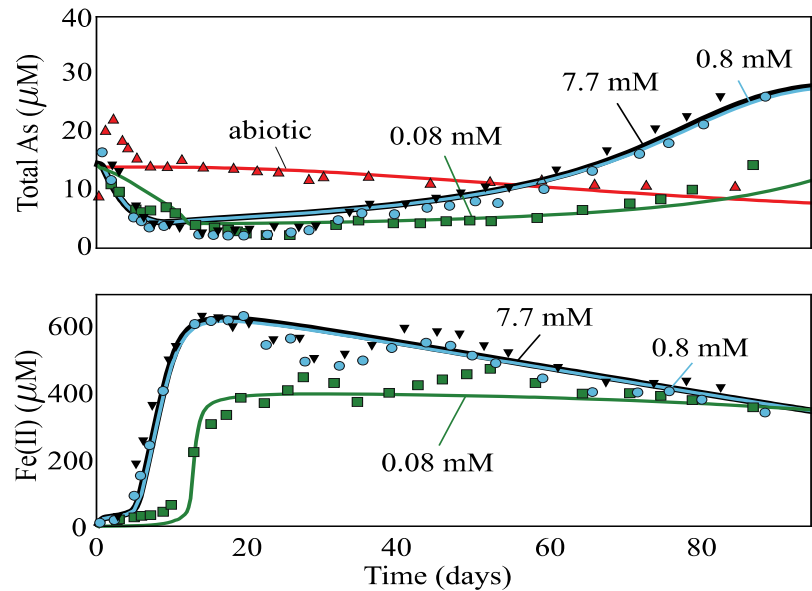


- Magnetite formation rate depends strongly on concentration of surface-complexed Fe^{2+}
- Rate decreases as a result of passivation effects



[Rawson et al., 2016, *ES&T*]

New Insights from Numerical Modeling



[Rawson et al., 2016, *ES&T*]

Key to replicate all aqueous/solid phase observations for all 4 columns:

- Sorption to newly formed magnetite is insufficient to explain As attenuation
- Good match with data relies on incorporation of released (desorbed) As into magnetite (co-precipitation) or formation of surface precipitates



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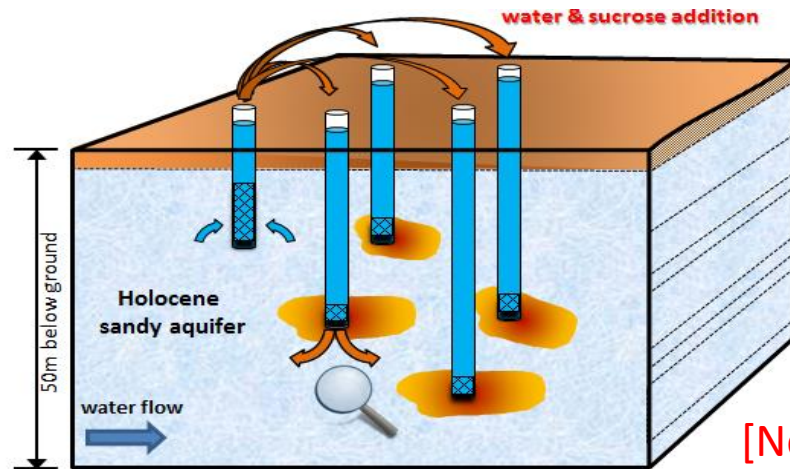
eawag
aquatic research ooo



EBERHARD KARLS
UNIVERSITÄT
TÜBINGEN

**Modeling Processes Governing Arsenic mobility during a Sucrose
Injection Experiment in a West Bengal Plain Aquifer**

Field-Scale Sucrose Injection Experiment (West Bengal Plain): Experimental Setup



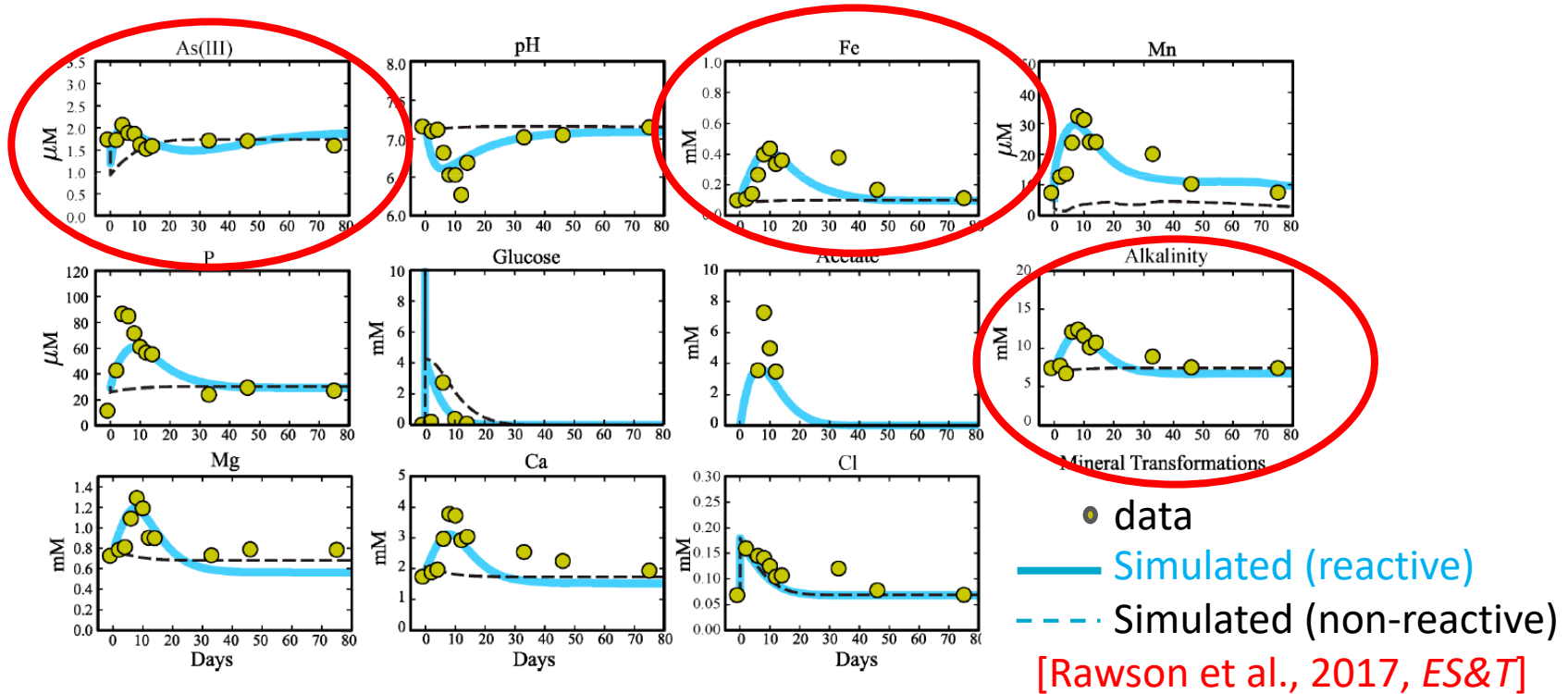
[Neidhardt et al., 2014, *Chem. Geol.*]

- Brief sucrose injection into 4 wells at different depth
- Slow natural groundwater flow
- Aquifer: Anoxic, no nitrate, no sulphate

Iron reduction is the clearly main redox process

- Monitoring for 150 days

Numerical Modelling of Sucrose Injection Experiment



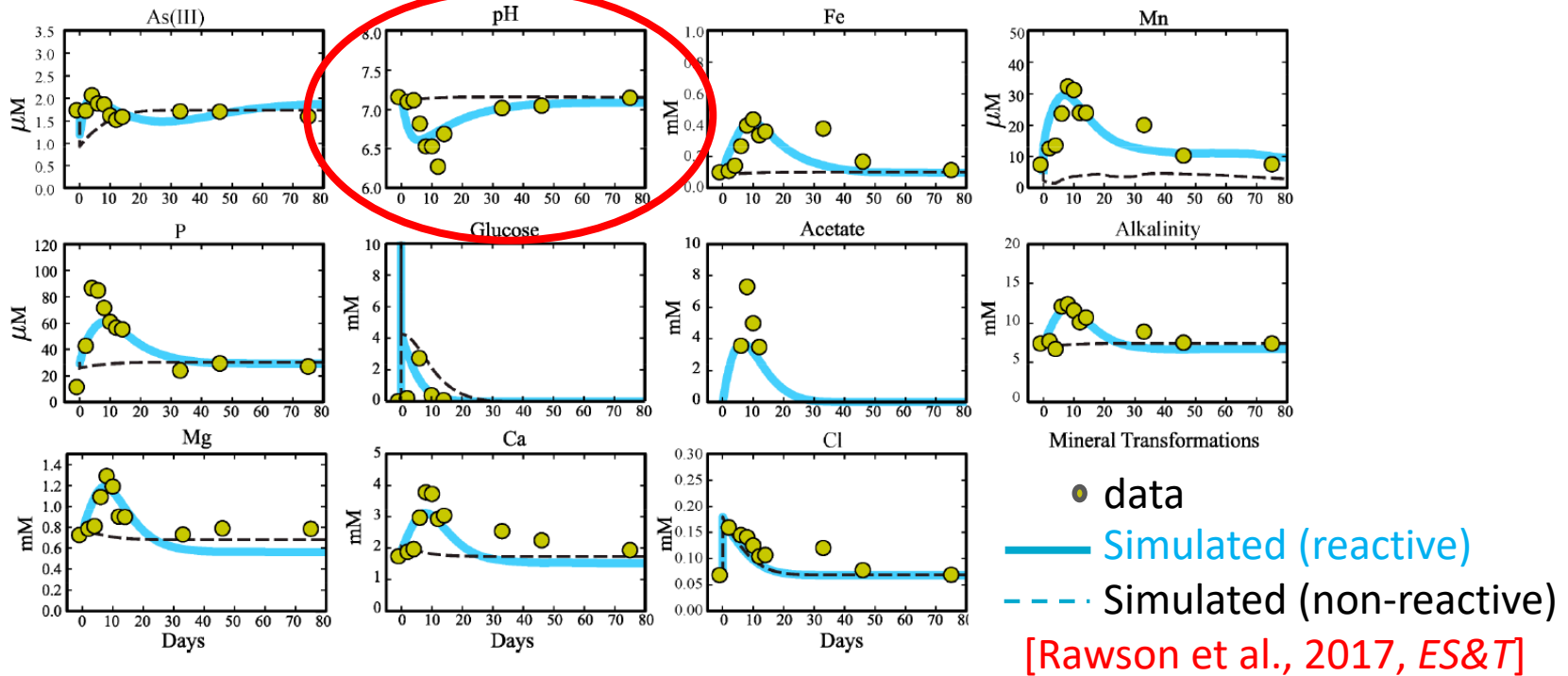
- Sucrose injection stimulated rapid reductive dissolution of Fe-oxides

HCO_3^- and Fe increase

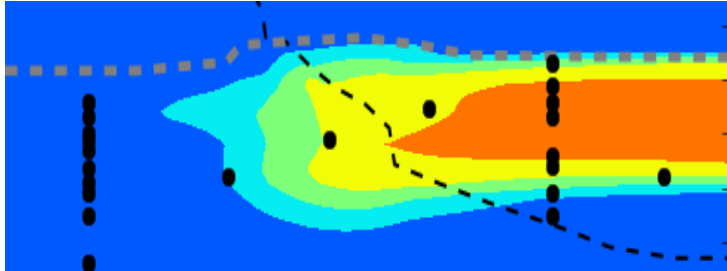
Surprisingly minor/modest increase of As !

- Sucrose transformation to acetate and temporary pH drop

Main Insights from Reactive Transport Modelling



- Temporary pH change affects As partitioning – explained by surface complexation model
- Conceptual/numerical model developed for column study (largely) holds for controlled field study: **As incorporation during Fe mineral transformation important to match data**



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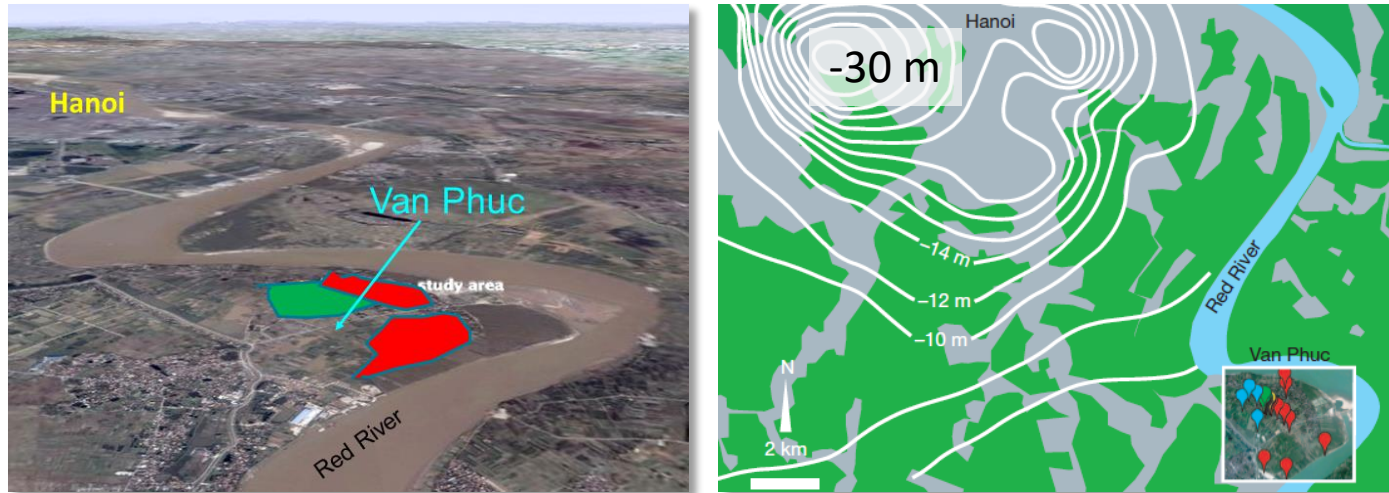


eawag
aquatic research ooo

Ilka Wallis, Flinders University
Henning Prommer, CSIRO Land and Water / UWA
Jing Sun, UWA
Adam Siade, UWA
Michael Berg, eawag
Rolf Kipfer, eawag

Field-scale modeling of arsenic release and migration at Van Phuc, Vietnam

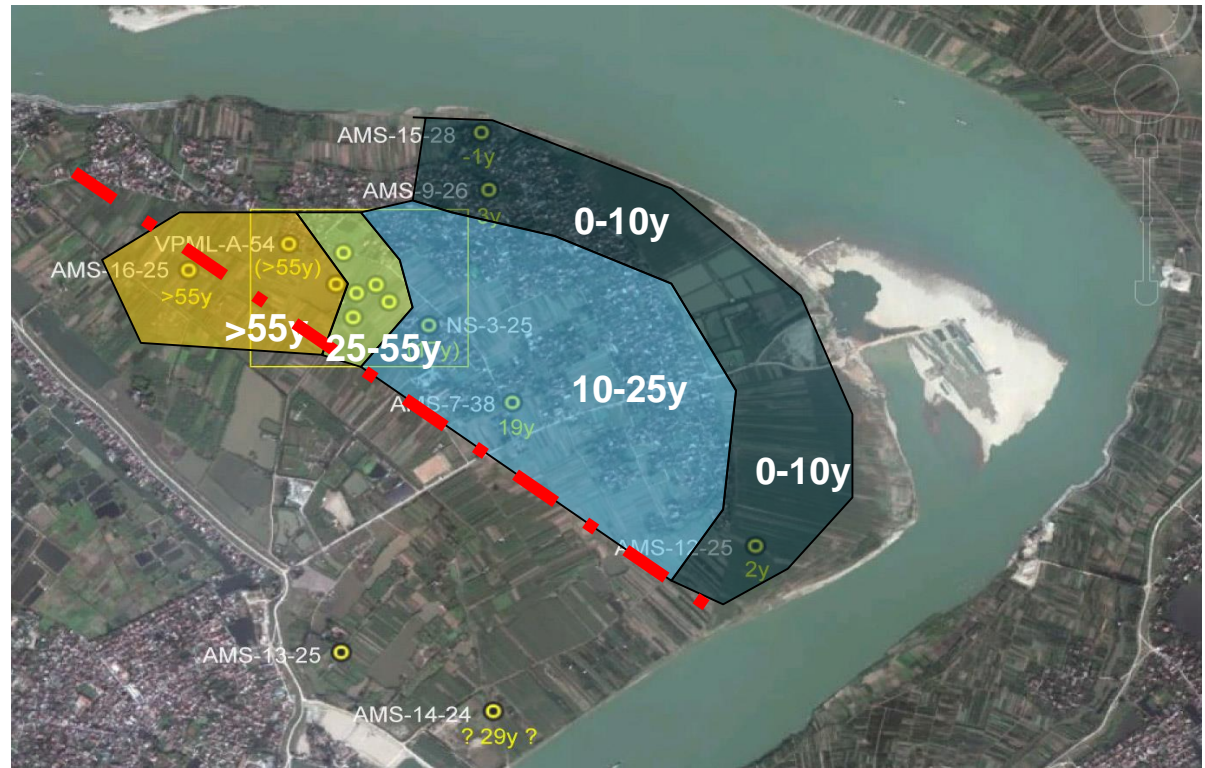
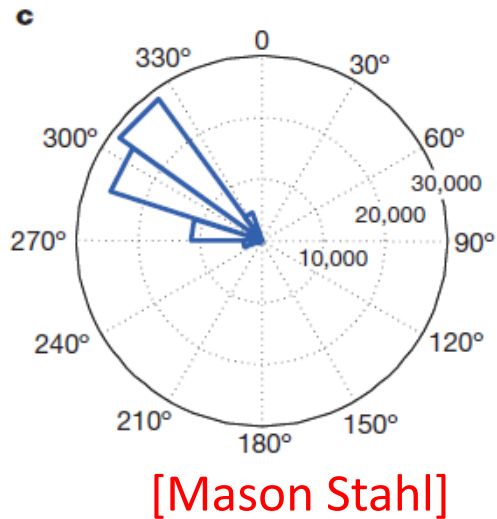
Regional Groundwater Flow



[Van Geen et al., 2013, Nature]

- Regional groundwater flow driven by large-scale groundwater abstraction in Hanoi
- Locally groundwater depletion rate up to 0.2–0.6 m/year

Van Phuc Transect Study

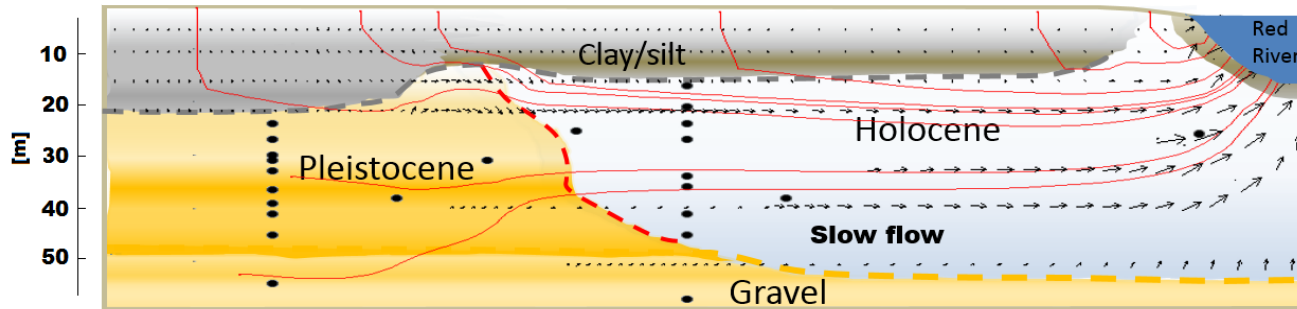


[Rolf Kipfer, eawag]

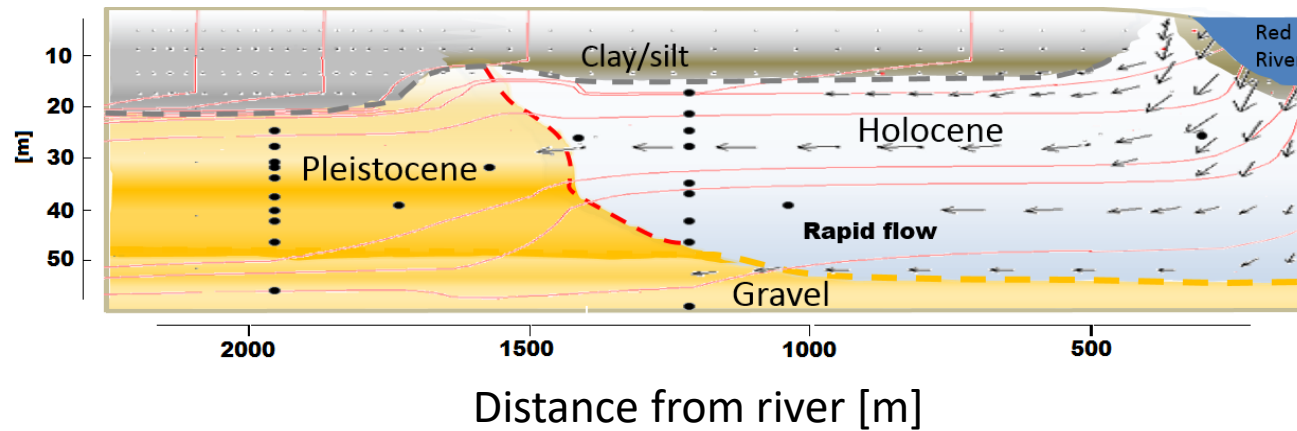
- Head data indicate stable flow direction
- Tritium/Helium data constrain flow rates

Conceptual Hydrogeological Model

- Pre 1950s: Slow groundwater flow from NW → SE



- Post 1950s: Pumping-induced reversal of flow



Van Phuc Reactive Transport Modeling Study

- Integration and joint interpretation of flow, environmental tracer, multi-component 'macro'-chemistry and arsenic data
- Testing and refinement of conceptual model of As mobilisation and migration
- Stepwise approach:

Calibration of flow/transport patterns constrained by tritium/helium data

Development/calibration of reactive transport model

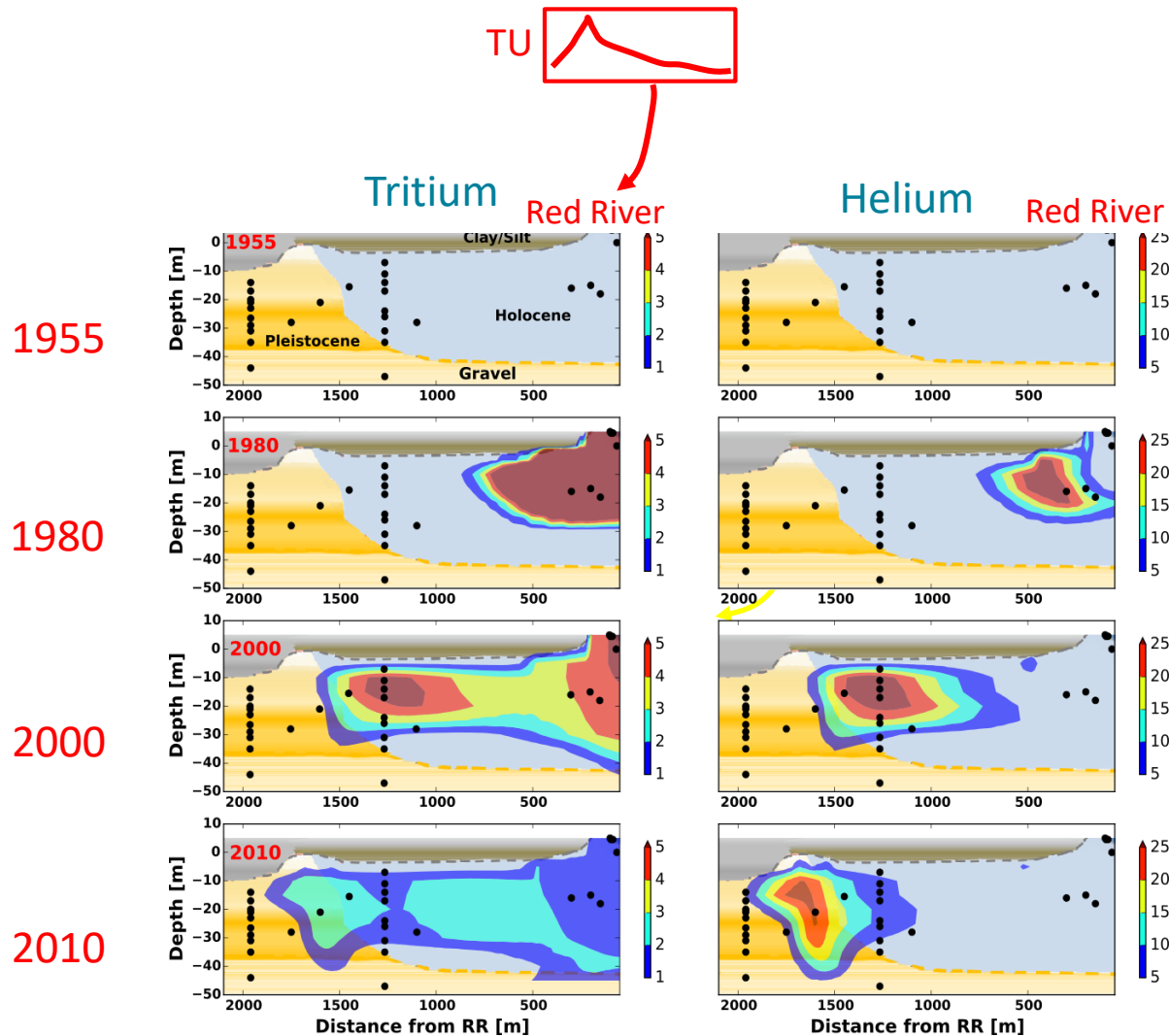
Key elements of reaction network:

Redox processes driven by DOC/SOM, including Fe-oxide reduction

Secondary mineral reactions

Surface complexation reactions of As and competing ions

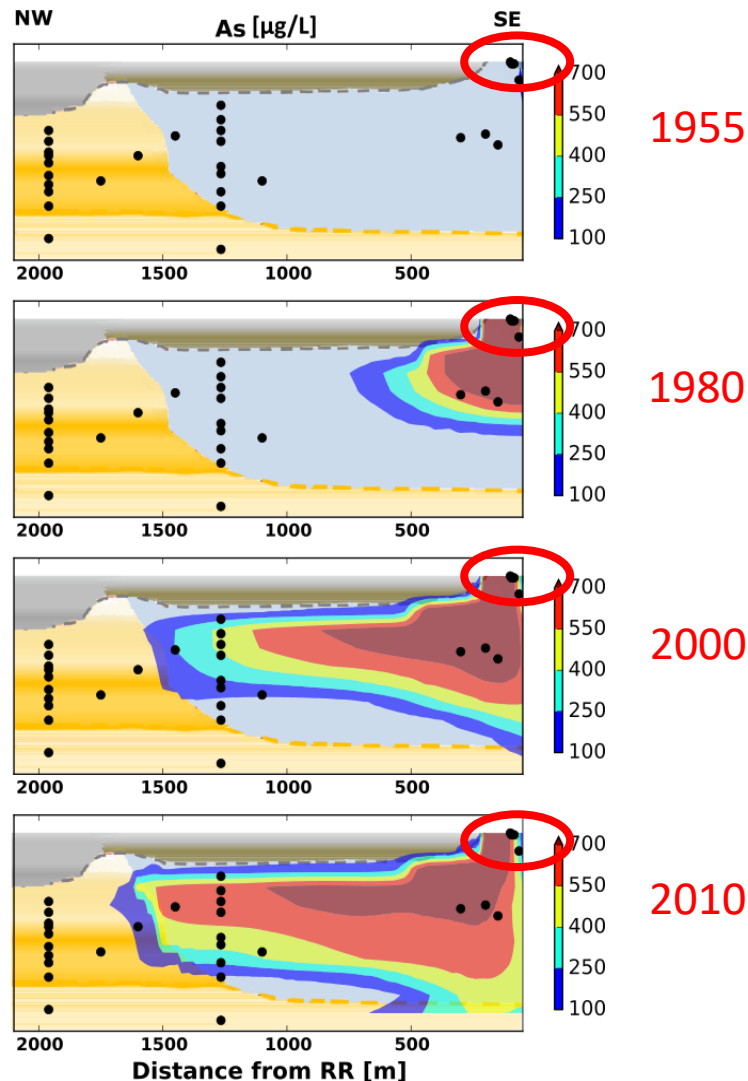
Flow and Environmental Tracer Transport Model



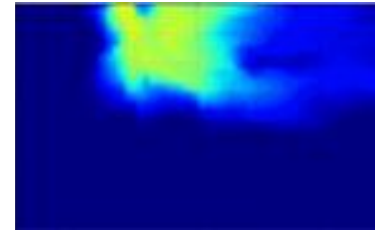
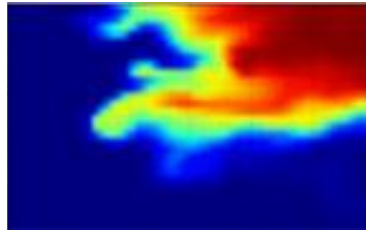
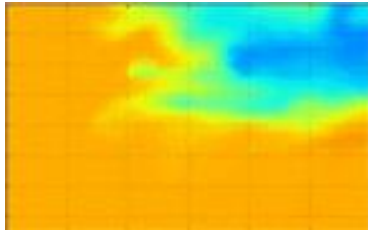
- Simulation period: 60 years (~Since start of pumping - 2010)
- Transient flow: Head gradient increases steadily
- Transient input of tritium at river; $T \rightarrow {}^3\text{He}$ half-life = 12.3 years
- Measured $T/{}^3\text{He}$ values from 2010 used to constrain model

[Wallis et al., under revision]

Reactive Transport Model: Simulated Fate of Arsenic



- Pumping-induced intrusion of river water: River muds act as 'biogeochemical reaction hotspot'.
- Electron acceptors O_2 , NO_3 and SO_4 and also DOC are 'instantly' consumed in the river muds.
- Majority of As is released at the river/gw interface in conjunction with Fe-oxide reduction + desorption
- Negligible reductive dissolution in the entire Holocene aquifer
- 70% of As plume mass derived at river (100% in 1955)
- 30% of As plume mass derived from As desorption, particularly due to elevated P (0% in 1955)



Arsenic Immobilization via In Situ Magnetite Formation

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Adam Siade, UWA

Benjamín Bostick, Lamont Doherty Earth Observatory

Steven Chillrud, Lamont Doherty Earth Observatory

Brian Mailloux, Barnard College

Yan Zheng, SUSTech and Lamont Doherty Earth Observatory



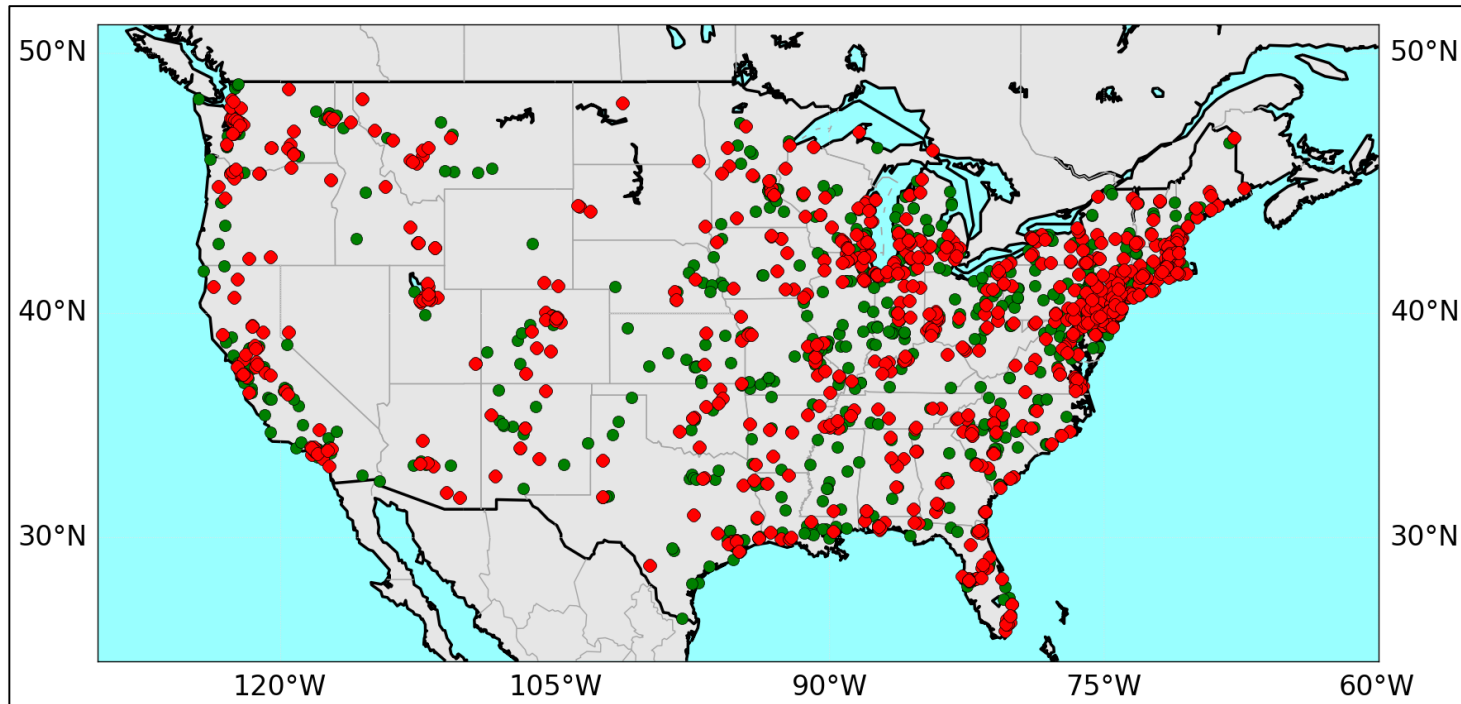
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Lamont-Doherty Earth Observatory
COLUMBIA UNIVERSITY | EARTH INSTITUTE

Columbia University NIEHS Superfund Research Program

Arsenic at US Superfund Sites

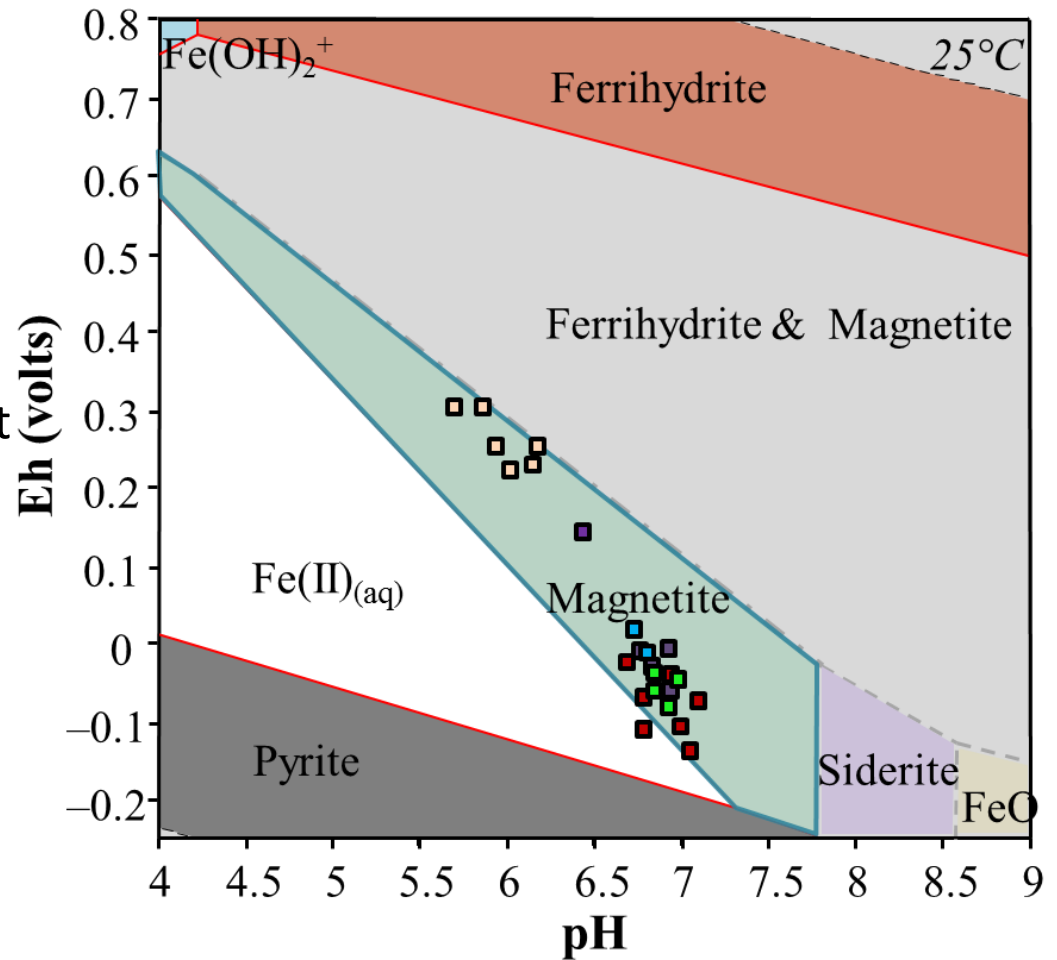


[CERCLIS Public Access Database]

- US National Priority List (i.e., “Superfund”) Sites (N=1767)
- US NPL Superfund Sites having As contamination (N=823)

Background: Magnetite-Based In Situ Remediation

- Many As-contaminated Superfund sites are co-contaminated with organic pollutants
- Redox conditions at many As contaminated Superfund sites suggest that ferrihydrite might be unstable
- Magnetite (Fe_3O_4) has a relatively **large stability field**. Retains As by co-precipitation and adsorption.



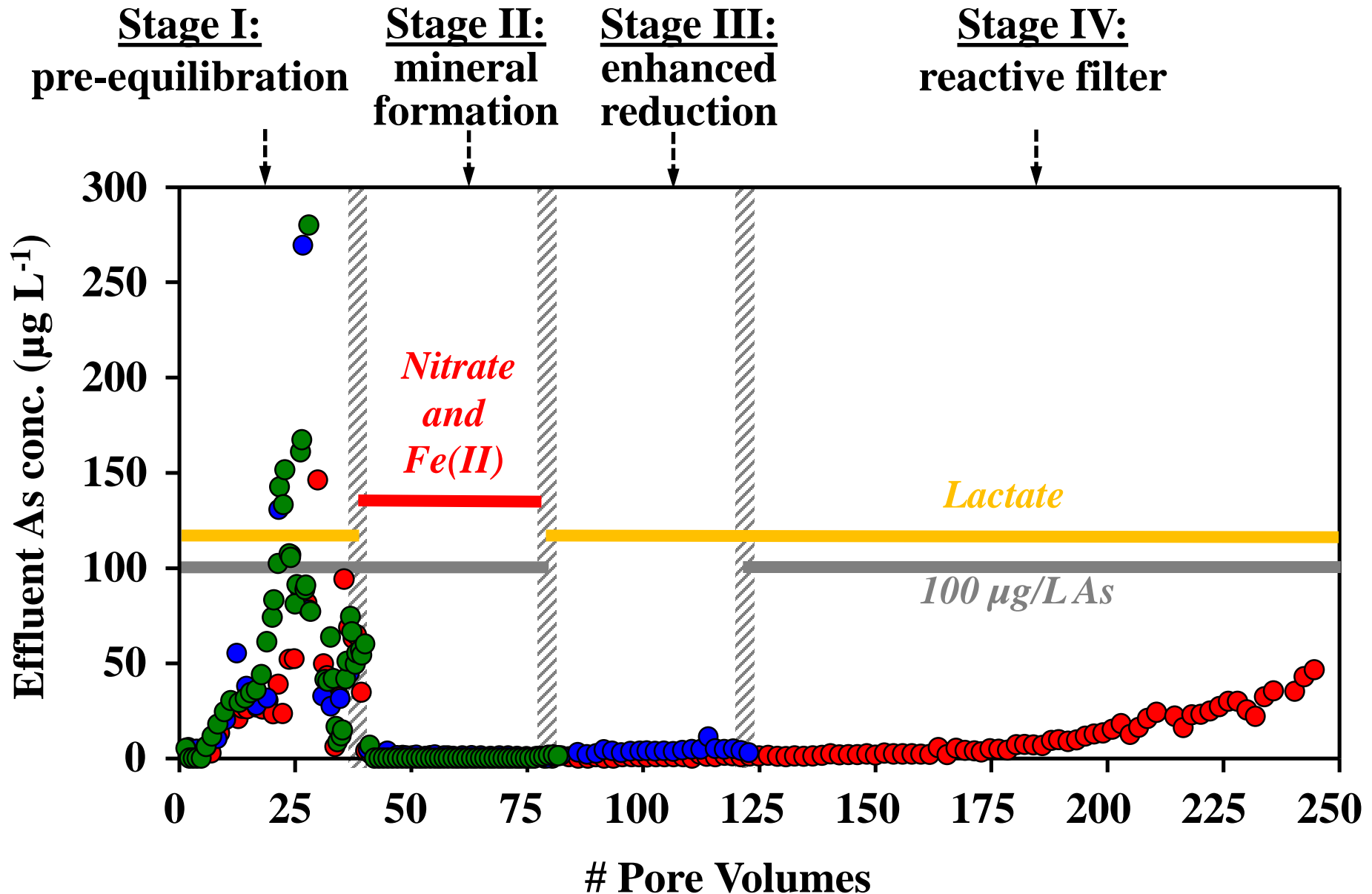
Four-Stage Column Experiment (Lamont Doherty Earth Observatory)



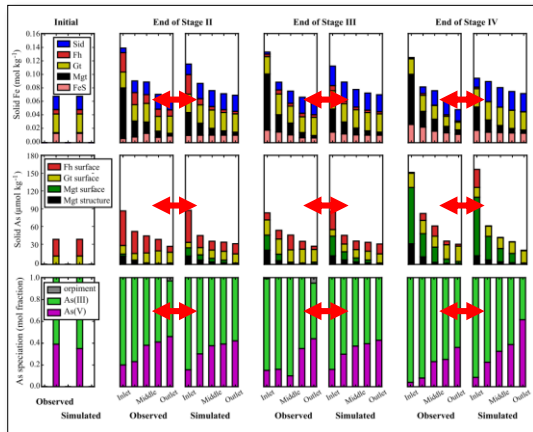
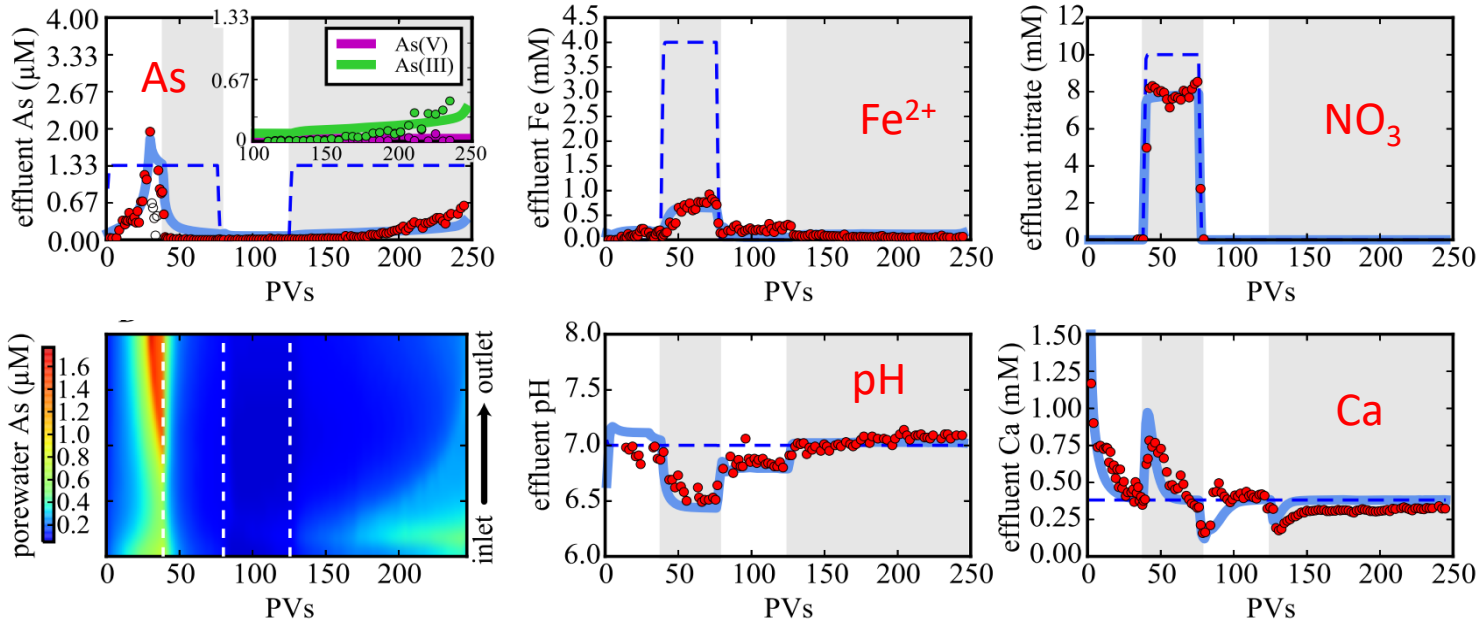
[Sun et al., 2016, *ES&T*]

- 1 Quartz sand column
- 3 Dover landfill sediment columns
- 125 days / 250 PV, subdivided into 4 stages

Four-Stage Column Experiment (Lamont Doherty Earth Observatory)



Arsenic Immobilization via In Situ Magnetite Formation



- Matching all **aqueous + solid phase** data collected during laboratory experiments requires rather complex (but highly plausible) reaction network

[Sun et al., 2018, *ES&T*]

Key Elements of Final Reaction Network

- Reductive dissolution of existing (Dover) ferrihydrite during lactate-amended phases
- Reductive dissolution of goethite neglected
- Mineral precipitation and transformation
 - neo-formed ferrihydrite + magnetite
 - siderite + mackinawite precipitation
- Surface complexation reactions with 3 types of sites
 - low sorption site density on (Dover) ferrihydrite
 - lower sorption site density on (Dover) goethite
 - high sorption site density on neo-formed ferrihydrite
- pH buffering by calcite dissolution
- Cation exchange (affecting Ca and Fe BTCs)

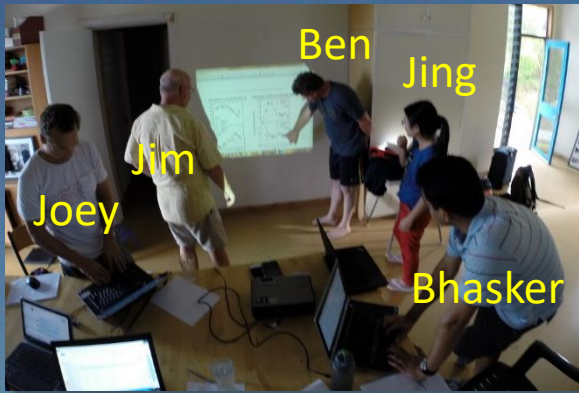
From Bench-Scale Research to Field Application



- First successful push-pull tests in Yinchuan (China) – collaboration with SUSTech, Shenzhen (modelling in progress)
- Upcoming field trial in October at coastal As-contaminated site in Italy – coordinated by La Sapienza University, Rome

Concluding Remarks

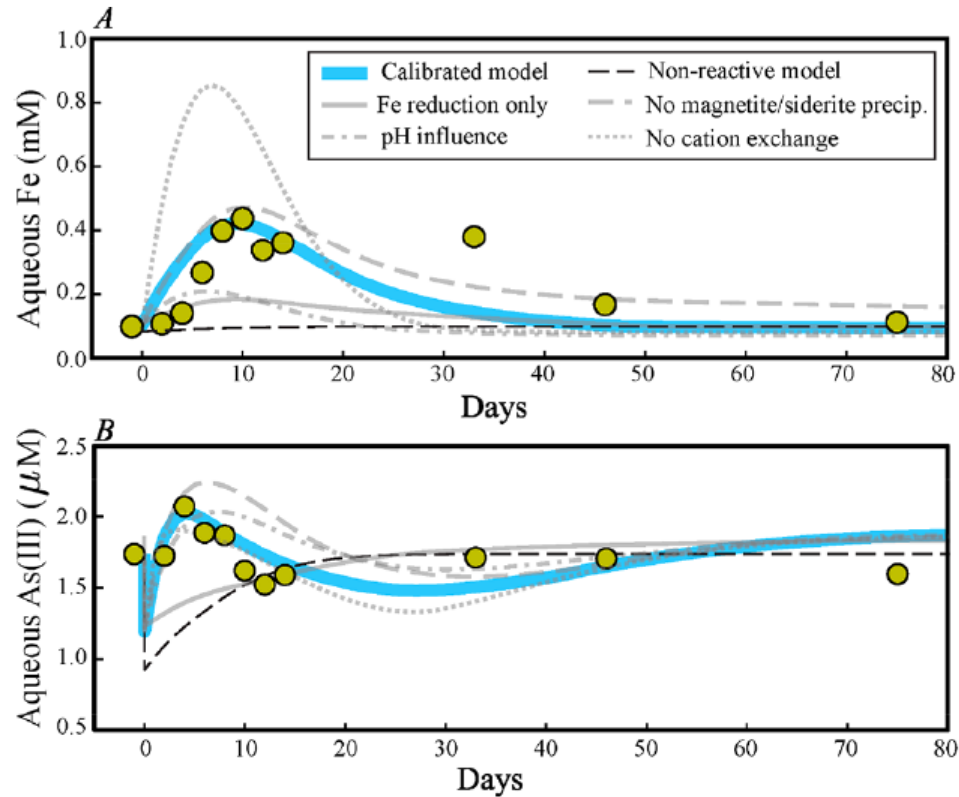
- Arsenic mobilisation associated with reductive dissolution of Fe-oxides is accompanied by a set of complex secondary geochemical reactions that impact As fate, for example
 - iron mineral transformations
 - pH change during sucrose degradation
- Identification and model-based quantification of the secondary reactions helps
 - to better understand laboratory and field-scale observations
 - design remediation methods
- Field-scale reactive transport modelling of geogenic arsenic will remain a significant challenge as many different geochemical factors affect 'As plume behaviour'
- Field-scale: Measured data generally provide only concentration snapshots that do not document temporal hydrochemical evolution
 - Use of environmental tracer data can provide important constraints



Thank you !



Process Identification



- Comparison of model variants to study which processes have contributed to As release and attenuation

[Rawson et al., 2017, *ES&T*]