Numerical modeling of arsenic mobility during reductive iron-mineral transformations

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ABSTRACT

Millions of individuals worldwide are chronically exposed to hazardous concentrations of arsenic from contaminated drinking water. Despite massive efforts towards understanding the extent and underlying geochemical processes of the problem, numerical modeling and reliable predictions of future arsenic behaviour remain a significant challenge. One of the key knowledge gaps concerns a refined understanding of the mechanisms that underlie arsenic mobilization, particularly under the onset of anaerobic conditions, and the quantification of the factors that affect this process. In this study, we focus on the development and testing of appropriate conceptual/numerical model approaches to represent and quantify the reductive dissolution of iron oxides, the concomitant release of sorbed arsenic and the role of iron mineral transformations. The initial model development in this study was guided by data and hypothesized processes from a previously reported,¹ well-controlled column experiment in which arsenic desorption from ferrihydrite coated sands by variable loads of organic carbon was investigated. Using the measured data as constraints, we provide a quantitative interpretation of the processes controlling arsenic mobility during microbial reductive transformation of iron oxides. Our analysis suggests that the observed arsenic behaviour is primarily controlled by a combination of reductive dissolution of ferrihydrite, arsenic incorporation into or co-precipitation with freshly transformed iron minerals and partial arsenic redox transformations.

Keywords: *arsenic, reactive transport, iron mineral transformations, surface complexation*

44 Introduction

45 Millions of humans worldwide are exposed to the consumption of groundwater contaminated with
46 arsenic concentrations that exceed the World Health Organization's acceptable drinking water limit of
47 10 $\mu\text{g/l}$.² Chronic exposure of humans to high concentrations of arsenic in drinking water is associated
48 with skin lesions, peripheral vascular disease, hypertension, black foot disease and a high risk of
49 cancer.³ Under oxidizing aquifer conditions, at circum-neutral pH, arsenic generally does not pose a
50 significant threat to groundwater resources as it strongly sorbs onto iron oxide minerals such as
51 ferrihydrite.² However, the intrusion of reactive organic carbon from sources such as carbon-rich
52 sediments, constructed ponds, recent degradation of plants, and wastewater^{2,4,5} has in the meantime been
53 identified as triggers for microbially mediated reductive dissolution of these iron phases, accompanied
54 by the release of ferrous iron and trace elements such as arsenic. The latter occurs on one hand, due to
55 the loss of the sorption capacity associated with the dissolution of the iron oxides,^{2,5-10} and additionally,
56 although to a lesser extent, due to competitive desorption by the bicarbonate generated during oxidation
57 of organic carbon.^{2,11-13} Among a range of conceptual models, arsenic release triggered by reductive
58 dissolution of iron oxides has evolved as the most widely accepted cause for the widespread presence of
59 arsenic in S/SE Asia groundwater, even though locally other mechanisms may also be responsible.
60 Additionally, associated with the redox transformations induced by labile organic carbon, arsenate
61 transforms to arsenite, which has in many instances been reported to sorb less strongly to iron oxides
62 compared to arsenate^{2,5,14-16} and thus appears to explain the often observed increased arsenic mobility in
63 reducing environments. Contradicting this view, various batch studies showed that at neutral pHs, which
64 are typical of many natural environments, arsenite sorbed to a similar or greater extent than arsenate on
65 hydrous ferric oxide and goethite.¹⁷⁻¹⁹ However in these studies the sorbed arsenic concentrations were
66 unrealistically high compared to natural environments and in one of the studies the lowest of three
67 sorbed arsenic concentrations showed the reverse with approximately 30% more arsenate sorbed than
68 arsenite at pH 7¹⁷, highlighting the possible variations in the observed behavior.

69

70 Further complexities in terms of understanding arsenic mobility arise where elevated concentrations of
71 dissolved ferrous iron promote a range of important iron mineral transformations towards more reduced
72 and/or more stable iron phases. A number of recent studies^{1,20-22} suggest that understanding how newly
73 formed iron minerals provide new sorption sites, with varying sorption capacities,¹⁷ that facilitate the
74 attenuation of arsenic, is a key issue for understanding arsenic mobility. Furthermore, the possibility of
75 the transformation reaction to incorporate arsenic into the iron mineral structure may also contribute to
76 arsenic attenuation.^{23,24} Experiments concerning the dissimilatory iron reduction of the common iron
77 oxide, ferrihydrite, have shown transformations to goethite and lepidocrocite at low ferrous iron
78 concentrations, and also to magnetite, at high ferrous iron concentrations.^{21,25-27} A limited number of
79 studies have successfully quantified iron oxide transformations in numerical models.^{21,26,28} However,
80 despite the apparent significance of these processes for controlling concentrations and mass fluxes of
81 arsenic under both natural conditions and in environments requiring remediation, they have yet to be
82 considered in the development, testing and application of numerical modeling frameworks for such
83 systems.

84

85 Therefore, this study was aimed at developing and evaluating a range of numerical modeling approaches
86 that can suitably quantify the role of the key geochemical processes associated with a subset of iron
87 mineral transformations and their impact on arsenic mobility. Our initial model development was guided
88 by experimental data and hypothesized processes that were derived from well-controlled column studies
89 in which arsenic mobilization from ferrihydrite-coated sands, by variable loads of lactate, was studied.¹
90 Subsequently, a series of alternative conceptual models were investigated. Those alternative models
91 explore the impact of arsenic incorporation with magnetite and the (partial) oxidation of arsenite.^{23,24}
92 For each model variant, model parameters were estimated through a calibration procedure using Particle
93 Swarm Optimization (PSO).²⁹⁻³¹

94

95 **Materials and Methods**96 ***Data Set Description***

97 The model development was guided by a comprehensive data set collected during the laboratory column
98 study of Tufano and Fendorf.¹ In their study, arsenic mobilization was investigated under both abiotic
99 and microbially induced iron-reducing conditions. Four columns were packed with ferrihydrite coated
100 quartz sand (iron content 83 mmol kg⁻¹) loaded with arsenite in an anaerobic chamber (initial loading
101 concentration of 4.48 mmol kg⁻¹) and inoculated with an iron reducing bacteria, *Shewanella*
102 *putrefaciens* strain CN-32. The effective porosity of the column filled with ferrihydrite-coated sands
103 was determined to be 0.48. An artificial groundwater solution was pumped from the bottom up through
104 each of the four columns at a rate of 6.8 $\mu\text{L min}^{-1}$, corresponding to ~ 3 pore volumes per day. Three of
105 the four column influent solutions contained lactate at concentrations of 7.7 mM, 0.8 mM, and 0.08
106 mM, respectively. A buffer (PIPES) was used to maintain a pH of 7.1. Water samples were analyzed
107 periodically over a 90 day period for effluent concentrations. In addition to the columns that were
108 analyzed for aqueous concentrations, triplicate columns were run simultaneously and sacrificed after 11,
109 52, and 90 days respectively to analyze the iron mineralogy. Following on from this earlier work the
110 present study focuses on the development of a suitable reactive transport modeling approach and its use
111 for an in-depth data interpretation.

112

113 ***Modeling approach and tools***

114 In the first step, the geochemical model PHREEQC-2³² was used to model and reconstruct the initial
115 water, sediment and surface concentrations that prevailed within the columns at the start of the column
116 experiments. In parallel, a simple 1D flow model representing the column setup was constructed with
117 the USGS model MODFLOW.³³ The flow model and the simulated initial concentrations formed the
118 basis for the subsequent transport simulations with the reactive multi-component transport code
119 PHT3D,³⁴ which couples the transport simulator MT3DMS,³⁵ and PHREEQC-2. A PSO code was

written within the PEST++ YAMR run manager³⁶, and linked with PHT3D, in order to estimate adjustable model parameters. The sum of squared residuals between measured and modeled concentrations was minimized for each investigated model variant, subject to the constraint that model parameters agree with their corresponding values published in the literature as closely as possible. The PSO calibration procedure was also used to address posterior parameter uncertainty for the chosen conceptual model (see Supporting Information).

Conceptual model of biogeochemical processes and reaction network implementation

The reactive processes within the columns leading to arsenic release/attenuation were developed with a focus on five key processes (i) arsenic desorption by chemical disequilibrium during pore water replacement, (ii) sorption of arsenic on (freshly) transformed iron phases, (iii) arsenic release during reductive dissolution of iron (iv), partial oxidation of arsenite to arsenate, and, (v) arsenite incorporation with magnetite.

Four main conceptual models (*S1-S4*) were identified and further refined and investigated through varying the contributions of specific processes. They were translated into numerical models by formulating a mix of equilibrium and kinetically controlled reactions. These four main conceptual models, reported variants and the corresponding numerical model implementations are listed in Table 1.

Modeling of initial experimental conditions

Using PHREEQC-2 in batch mode phosphate and arsenic were sequentially pre-sorbed onto the ferrihydrite coated sand. Arsenite and arsenate were decoupled from the overall redox equilibrium and redox transformations were assumed to be kinetically controlled (see also Wallis et al.³⁷). To simulate sorption to mineral surfaces an electric double layer surface complexation model in accordance with Dzombak and Morel³⁸ was employed. However, whilst keeping the Dzombak and Morel³⁸ database unchanged, the surface site densities of ferrihydrite (weak and strong site) were iteratively adjusted to

eventually attain the measured $0.84 \mu\text{mol kg}^{-1}$ and $4.48 \text{ mmol kg}^{-1}$ of phosphate and arsenic surface loadings, respectively, while the ratio between weak and strong sites was kept constant. Phosphate was considered in the surface complexation simulations due to its known, strong affinity for sorption and the potential for competition with both arsenite and arsenate.^{39,40} The modeled initial water chemistry that was derived through this procedure was utilized to define the initial conditions (Table SI1) for the reactive transport model simulations.

Reductive dissolution of iron

In all investigated numerical model variants, the key reaction in the biotic experimental columns was the oxidation of lactate (electron donor) coupled to the reduction of ferrihydrite (electron acceptor):

Note, that ferrihydrite is here, both for simplicity and to represent natural variation, represented as $\text{Fe}(\text{OH})_3$, while recent work by Michel et al.⁴¹ suggests a stoichiometry $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$ for ferrihydrite in its pure form. To account for the kinetic control of the reaction the lactate degradation rate R_{lac} is described by a standard Monod-type rate expression:

$$R_{lac} = \alpha \left(\frac{[\text{Fe}(\text{OH})_3]}{k_{ferri} + [\text{Fe}(\text{OH})_3]} \right) \left(\frac{C_{lac}}{k_{lac} + C_{lac}} \right) \quad (2)$$

where α is a rate constant, $[\text{Fe}(\text{OH})_3]$ and C_{lac} are the concentrations of ferrihydrite and lactate, and k_{ferri} and k_{lac} are the half saturation constants for ferrihydrite and lactate, respectively.

Iron mineral transformations

Within the columns, EXAFS spectroscopy demonstrated that during the experiments a partial transformation of ferrihydrite to magnetite occurred. This was attributed to the reductive dissolution of ferrihydrite, which produces ferrous iron. Based on the findings of Hansel et al.^{21,42} and Tufano et al.²⁶ it was assumed that when dissolved ferrous iron occurs in excess of $2 \times 10^{-4} \text{ mol L}^{-1}$ it starts to catalyze the re-crystallization of $\text{Fe}(\text{II})$ to magnetite via a solid state conversion of the surface of ferrihydrite. The

originally proposed rate expression for magnetite precipitation of Tufano et al.²⁶ was modified and a term was added that allows for the limitation of available surface sites.⁴³

$$R_{magn-ppt} = -k_{magn-pptn} \max \left(0, \left[1 - \frac{K_{sp(magn)}}{IAP_{magn}} \right] \right) \left(\frac{[Fe^{2+}]}{K_{magn-pptn}^{thres(Fe^{2+})} + [Fe^{2+}]} \right)^x \left(0, \frac{[Fe(OH)_3] - C_m}{[Fe(OH)_3]} \right) \quad (3)$$

where $k_{magn-pptn}$ is the effective rate coefficient, determined through model calibration, IAP_{magn} is the ion activity product of the aqueous solution, $K_{sp(magn)}$ is the solubility product for magnetite, $K_{magn-pptn}^{thres(Fe^{2+})}$ is a threshold term describing the aqueous concentration of $[Fe^{2+}]$, which requires an exponential term (x) set at 3, $[Fe(OH)_3]$ is the concentration of ferrihydrite and C_m is the ferrihydrite concentration at which magnetite precipitation effectively stalls.

Arsenite incorporation with magnetite

The possibility of arsenite accumulation via precipitation was considered in model variants *S2* and *S4* since a number of studies have observed decreasing aqueous arsenic concentrations while Fe mineral transformations occurred.^{23,44} Furthermore, Wang et al.⁴⁵ analyzed the interaction of As(III) with magnetite during its precipitation at differing As/Fe ratios. They characterized the samples using EXAFS spectroscopy to identify whether the uptake was via adsorption or precipitation; at lower ratios the uptake of As(III) was predominately a result of sorption, while at higher ratios (As/Fe 0.333) the formation of a surface precipitate became increasingly dominant. The stoichiometry of the reaction was assumed to be:

The rate of the reaction was directly connected to the magnetite formation rate described by Eqn. (3), while varying its relative importance, i.e., different molar ratios of As:Fe between a lower limit of 1:100 and an upper limit of 1:0.6, were tested and evaluated.

Arsenic surface complexation reactions

193 Sorption of arsenic was assumed to occur in all model variants (*S1-S4*) as (i) surface complexation
194 reactions with ferrihydrite and (ii) as surface complexation reactions with the newly formed magnetite.
195 An electrostatic double layer model based on Dzombak and Morel's³⁸ surface complexation reactions
196 for arsenite, arsenate, and phosphate sorption onto ferrihydrite were used in the simulations. The model
197 was extended to utilize Dixit and Hering's¹⁷ arsenite sorption reactions onto magnetite and associated
198 surface site densities. Note, that while various sorption site densities of ferrihydrite and magnetite were
199 tested, the total number of sorption sites was stoichiometrically linked with the temporally varying
200 mineral concentrations. Other sorption reactions incorporated were ferrous iron, phosphate,⁴⁶ and
201 bicarbonate,¹² which introduced competitive sorption between arsenic and other ions for a finite number
202 of sorption sites. The stoichiometries of the considered surface complexation reactions are listed in
203 Table 2.

204

205 *Arsenite oxidation*

206 To investigate a range of different potential explanations for the observed As behaviour, a subset of the
207 simulations (*S3* and *S4*) incorporated the previously not considered possibility that some
208 arsenite/arsenate redox transformations have occurred. Initially, we tested the possibility that the
209 arsenite that was added during the preparation of the columns was oxidized to arsenate at varying
210 degrees shortly after sorbing on the ferrihydrite-coated sands. While the prerequisites for such an
211 oxidation to occur were considered to be reasonably unlikely, a partial, photo-induced⁴⁷ oxidation or an
212 oxidation via intermediate Fe(III) phases was reported elsewhere⁴⁸ for a Fe(III)-goethite system.

213

214 *Arsenate reduction*

215 While arsenite and arsenate were decoupled from the overall redox equilibrium, kinetically controlled
216 arsenate reduction to arsenite was still assumed to occur in the three lactate-amended columns, except
217 for model variants *S1* and *S2*, which assumed that As persisted as arsenite throughout the entire

218 experiment. The rate expression describing this reaction was dependent on both arsenate and lactate
219 concentrations using a standard Monod-type expression:

$$R_{As(v)red} = \alpha \left(\frac{C_{aqu As(v)}}{k_{aqu As(v)} + C_{aqu As(v)}} \right) \left(\frac{C_{lac}}{k_{lac} + C_{lac}} \right) \quad (5)$$

220 where α is a rate constant, $C_{aqu As(v)}$ and C_{lac} are the concentrations of arsenite and lactate, and
221 $k_{aqu As(v)}$ and k_{lac} are the half saturation constants for arsenite and lactate, respectively.

222

223 ***Model development and calibration strategy***

224 The model development started with the numerical implementation of the initial conceptual
225 hydrochemical model of Tufano and Fendorf¹ (S1). A manual trial-and-error calibration procedure was
226 employed in order to provide a suitable set of initial parameter estimates for the subsequent automatic
227 calibration. This approach was repeated for the revised conceptual models in which initial arsenite
228 oxidation (S3, S4) and arsenic incorporation with magnetite (S2 and S4) was considered. The model
229 parameters associated with each variant of the numerical implementation were then estimated by
230 minimizing the sum of squared residuals between model-simulated and experimentally measured
231 results. The Gauss-Levenberg-Marquardt method was initially attempted, to further refine the model
232 parameters.⁴⁹⁻⁵¹ However, due to the severe nonlinearity of the inverse problem in this study,
233 convergence was difficult to achieve with this algorithm. Therefore, the heuristic PSO method was
234 implemented, which is known for its relatively high convergence rates (especially for Pareto analyses),
235 and its effectiveness at avoiding local minima,²⁹ which is a significant issue for severely nonlinear
236 optimization problems. The parameters to be estimated included a number of kinetic reaction rate
237 constants, arsenic surface complexation constants, and surface site densities associated with specific
238 iron minerals (Table 2). These parameters were largely interdependent of each other. Furthermore,
239 calibration was constrained to produce an arsenic surface loading of 4.25×10^{-5} M, corresponding to the
240 value measured by Tufano and Fendorf¹ as well as by pre-defined degrees of initial arsenite oxidation
241 (model variants S4a and S4b). Prior information, obtained from literature^{17,38,52} and expert knowledge,

was used to define the upper and lower bounds of each parameter, and subsequently to obtain an approximately Bayesian estimate of the parameters.

Results and Discussion

Reductive dissolution of ferrihydrite and fate of ferrous iron under varying lactate loads

For all investigated conceptual models, simulations reproduced the temporal concentration changes of iron that were induced by the amendment and transformation of varying lactate concentrations in conjunction with the reductive dissolution of ferrihydrite. Figure 1 shows selected, representative results for variant *S4b*. Similar results were, however, obtained for all other discussed model variants. In the three columns in which lactate was added, dissolved ferrous iron concentrations increased significantly until day 20 of the column operation. Larger and faster increases were associated with the addition of 7.7 mM and 0.8 mM compared to the addition of 0.08 mM, while virtually no difference was found between the addition of 7.7 mM and 0.8 mM lactate. The model replicated these observations closely once a suitable value for the half-saturation constant in the Monod term for lactate (Eqn. 2) was selected.

The results for all model variants are also consistent with the interpretation that the time lag in the breakthrough of ferrous iron at the column effluent is due to the retarded transport of ferrous iron that is freshly released during ferrihydrite dissolution. Breakthrough of the ferrous iron in the column effluent initially occurred only at low concentrations due to immediate re-sorption on ferrihydrite. However, once a new sorption equilibrium (corresponding to the higher aqueous ferrous iron concentrations) was attained throughout the column, i.e., newly released ferrous iron was no longer sorbed, a substantially higher breakthrough concentration was observed. This is illustrated in Figure 2, which shows simulated concentration profiles for model variant *S4b* for the 7.7mM lactate amendment cases at various times after the start of the experiment. Sorbed ferrous iron reached saturation at day 11, whilst in the case of 0.08mM lactate amendment a similar level of saturation was only reached after 19 days (Figure SI1).

Following the initial breakthrough of dissolved ferrous iron in the column effluent, the concentrations peaked quickly before decreasing successively (Figure 1). The decrease was more pronounced in the case of 7.7mM and 0.8mM than the 0.08 mM lactate amendment. The observed decreases can be replicated by the numerical model as a result of the successively lower rate of ferrihydrite dissolution within the column, which causes a slowing release of ferrous iron. This decrease is not outweighed by the simultaneous decrease in available sorption sites, which induces the release of ferrous iron.

Iron mineral transformations

The Fe-EXAFS results for the three lactate amended columns, as discussed in¹ showed that specifically in the early phase of the experiment (before day 11) ferrihydrite was partially transformed to magnetite (Figure 3) while, on the other hand, no magnetite was found in the abiotic column. No other iron minerals were identified by EXAFS spectroscopy, i.e., no goethite or lepidocrocite formed prior to magnetite. This may be due to the oxyanions (arsenite and phosphate) poisoning the transformation.^{53,54} The observations are in line with previous studies^{27,42} which have shown that in chloride-dominated systems, at neutral pH, with high ferrous iron concentrations magnetite is the primary transformation product of ferrihydrite. As shown in Figure 3, our calibrated model was able to closely replicate those observations. In the lactate amended columns the highest iron transformation rates occurred in the early phase of the experiments once the ferrous iron that was produced during reductive dissolution of ferrihydrite started to successively increase and exceed the set threshold concentration of $2 \times 10^{-4} \text{ mol L}^{-1}$ of Fe^{2+} . After an initial rapid increase of the magnetite formation rate, peaking after 5-6 days in the 7.7mM/0.8mM lactate columns, to 7-8 days in the 0.08 mM lactate column, the iron transformation rates decrease quickly, before stalling 7 to 12 days after the start of the experiments (see Figure 3). In the model, which closely replicated the fractions measured by Tufano and Fendorf,¹ this occurred when about 10% of the originally present ferrihydrite was consumed or transformed and the available sorption sites for magnetite formation had decreased accordingly. As magnetite consists of Fe(II) in octahedral sites and Fe(III) in both tetrahedral and octahedral coordination, the presence of tetrahedral Fe(III) at the

ferrihydrite surface controls the formation of magnetite.⁴³ Thus surface passivation may limit magnetite formation once tetrahedral Fe(III) surface sites have been exhausted.²⁷ Zachara et al.⁵⁵ also discussed that high bicarbonate concentrations may impede conversion of ferrihydrite to magnetite by minimizing site accessibility through bicarbonate sorption. In the column study, bicarbonate concentrations were not particularly high. However, the elevated concentrations of sorbed arsenic on the sites provided by ferrihydrite may have a similar effect on minimizing site accessibility and thus play a role on limiting the formation of magnetite.⁵⁶

301

Compared to the rate expression proposed by Tufano et al.,²⁶ a more process-based formulation for magnetite formation (Eqn 3) could potentially employ a rate-dependence on sorbed ferrous iron concentrations^{55,57} rather than the aqueous ferrous iron concentration. The impact of changing the rate expression was evaluated for the model of the 7.7mM lactate amended column. The results show that for a sorbed ferrous iron threshold concentration of $3.5 \times 10^{-3} \text{ mol L}^{-1}$, simulated aqueous and mineral concentrations remain similar to the results obtained when employing Eqn 3.

308

309 **Arsenic mobilization and attenuation**

310 ***Original conceptual model after Tufano and Fendorf (S1)***

Model simulations that were based on the reaction network implementation of the conceptual model proposed by Tufano and Fendorf¹ (S1), which assumed that all arsenic persisted as arsenite, allowed to mostly replicate the observed data of the abiotic (no lactate amendment) experiment after day 10 (Figure 4). Nevertheless, a deviation between the model and the observations persisted in that the simulations did not capture the initial effluent arsenite concentration drop that occurred prior to day 10. This discrepancy may be attributed to weaker outer-sphere arsenic complexes undergoing rapid desorption, a process that was not captured by our surface complexation model implementation.

318

For this model variant (*S1*), however, in the simulations of the lactate-amended columns, the experimentally observed arsenite breakthrough concentrations could not be reproduced. For example, in the column in which 7.7 mM lactate was amended, observed arsenic concentrations decreased dramatically during the first 12 days (Figure 4). In contrast to those observations, dissolved arsenite breakthrough concentrations increased significantly in all preliminary model simulations as a result of the lactate-induced reductive dissolution of ferrihydrite and the associated loss of sorption sites (Figure 4). Tufano and Fendorf¹ suggested that the observed sharp initial decrease in arsenic concentrations may be due to the newly generated sorption capacity of the freshly formed magnetite. This hypothesis was evaluated by successively increasing the sorption site density of the freshly precipitated magnetite. The simulations showed that a sorption site density of 3 mol per mol of magnetite would be required to replicate the observed concentration decrease. This is implausible as magnetite was previously estimated to have a 6 times lower specific surface area than ferrihydrite,¹⁷ which in the present study would correspond to approximately 0.02 mol per mol of magnetite, i.e., >120 times less than our model-estimated value. Furthermore sorption strengths of magnetite, as estimated by Dixit and Hering¹⁷ through a batch/modeling study, showed similar strengths (surface complexation constants) for both iron oxides and magnetite. Based on these modeling results it was concluded that it was unlikely that ‘classic’ equilibrium-type surface complexation reactions with magnetite could have been responsible for the observed decline in dissolved arsenic concentrations.

Revised conceptual models

Arsenic incorporation with magnetite (S2)

A key assumption of all initially investigated model variants was that arsenite was not allowed to be incorporated into the structure of magnetite during transformation. This was based on the findings of Coker et al.,⁵⁸ who concluded that arsenite could only exist as a surface complex. However a number of other column studies^{15,23,44} have observed enhanced arsenite retention in conjunction with iron transformations from ferrihydrite to magnetite. This suggests that the sink for arsenite may be

precipitation during ferrihydrite transformation to magnetite. Therefore model variants that allowed arsenite to be captured into the transforming magnetite were tested and evaluated for a range of different As:Fe molar ratios. This additional process was appended to the original model, and the calibration process was repeated with this model variant (S2). A relatively good representation of the observed arsenic and iron concentrations was achieved (Fig SI2). However to attain this, the molar ratio of As:Fe was 1:1.7. Furthermore, to achieve a satisfactory simulation of the observed arsenic breakthrough behaviour, the initial arsenic surface loading in the column had to be increased to 7.6×10^{-5} M compared to the 4.25×10^{-5} M reported by Tufano and Fendorf,¹ which further reduces the plausibility of this model variant.

Redox transformations of arsenite (S3)

Following from some initial test simulations of this conceptual model (see Supporting Information) this variant was formally calibrated (S3). The calibration procedure resulted in estimates of the (i) initial distribution of arsenite and arsenate (i.e., % of oxidation prior to start of the experiments), (ii) arsenic surface complexation reaction constants, (iii) surface site densities, (iv) kinetic reaction rate constants for ferrihydrite dissolution/magnetite precipitation and As(V) transformation to As(III) (Table 2). With the calibrated model it was possible to replicate all observed iron and arsenic concentrations from all four column experiments with a single, consistent model. This is illustrated in Figure SI3, which shows the comparison between the simulated and observed arsenic and ferrous iron breakthrough curves.

In the simulation of the abiotic column that shows a good agreement with the data, arsenic leaching from the column occurs in the majority as arsenate. However, in the simulations of the lactate amended model, the arsenate that was assumed to have formed during the experimental preparation was rapidly reduced to arsenite once the lactate reduction caused a shift to reducing conditions. The rapid transformation to arsenite in combination with the selected surface complexation constants that cause arsenite to sorb more strongly, causes the modeled effluent arsenic concentrations to successively

decrease within the first 20 days of the experiment (Figure 1). With reductive dissolution of iron progressing in the lactate-amended columns, the continuous loss of ferrihydrite-associated sorption sites causes arsenite to be released to the aqueous phase and effluent concentrations to steadily increase after day 20.

The key for this variant to match the experimental data is a parameterization of the surface complexation model that allows arsenite to sorb more strongly than arsenate. This agrees with the results of Dixit and Hering's¹⁷ batch experiments at circum-neutral pH. However, contradicting their observations, several column studies^{15,23,24} have demonstrated arsenite to desorb more extensively than arsenate.

Model including arsenic incorporation with magnetite and arsenite oxidation (S4)

In the final conceptual model variant, a combination of the previously discussed processes was implemented into the model. Two slightly differing variants (*S4a*, *S4b*) were considered, which depended on the degree of arsenite oxidation that was occurring and therefore defining the initial conditions. The first variant (*S4a*) assumed a partial arsenite oxidation of 25% (during the experimental setup) and the second variant (*S4b*) assumed it to be 10%. In each case, a good model fit was achieved, primarily by allowing variations in the ratio of arsenic incorporation with magnetite (relative to precipitating Fe). Assuming 25% and 10% arsenite oxidation (*S4a,b*), the simulated As:Fe molar ratio was 1:4.5 and 1:3.1, respectively, highlighting that a decrease in the assumed arsenite oxidation requires magnetite to more efficiently capture arsenite during the mineral transformation phase. However, with the increased As:Fe ratio the initial arsenic surface loading had to be increased slightly to 4.9×10^{-5} M (*S4a*) and even more to 6.2×10^{-5} M in *S4b*. Simulation results for *S4b* are displayed in Figure 1.

Assessment of model variants and implications

396 Our modeling framework that was developed in this study provides a process-based description of the
397 complex interactions that evolve during the reductive dissolution of ferrihydrite and its partial
398 transformation to magnetite. The model investigations provided the basis for the re-interpretation of
399 some well-controlled, previously reported experiments that attributed significant arsenic attenuation to
400 the adsorption on neo-formed magnetite. Among the original and revised conceptual/numerical models
401 the variant *S4* appears to be the most plausible variant. These variants capture the observed arsenic and
402 iron breakthrough dynamics for variable loads of lactate amendment best, suggesting that arsenic
403 incorporation with magnetite in addition to sorption on mineral surfaces must also have occurred and
404 contributed substantially to the attenuation of aqueous arsenic concentrations. Furthermore, based on the
405 model results, we speculate that a small fraction of the arsenite may have been oxidized prior or around
406 the start of the column operations. In the unlikely case that arsenite oxidation had occurred to a
407 significantly larger extent, it could still only explain the observed arsenic breakthrough curves if
408 arsenate sorption to ferrihydrite under the experimental conditions was weaker than arsenite sorption,
409 which contradicts several column experiments that suggested that arsenite had a higher mobility^{15,23,24}
410 compared to arsenate.

411

412 Eventually this implies that in the short term the intrusion and degradation of organic carbon and the
413 coupled reductive dissolution of ferrihydrite is not enhancing arsenic release until ferrihydrite and the
414 associated sorption capacity are nearing depletion. If indeed arsenic precipitation during magnetite
415 formation was the dominant process for attenuating arsenic concentrations, then iron oxide
416 transformations may limit or delay arsenic release into the groundwater. However, where reducing
417 conditions already prevail, iron transformations (for example to goethite) may have been completed and
418 thus no additional attenuation of arsenic occurs. Our results call for additional experiments that further
419 investigate whether arsenite was incorporated in the structure of the transforming magnetite or rather
420 accumulated as an amorphous As(III)/Fe(III) precipitate on the magnetite surface. Such experiments
421 could also further clarify whether the model-derived As:Fe molar ratios are plausible. In addition the

model framework should now be tested and extended for a variety of idealized laboratory conditions and for data sets from controlled and well-characterized field experiments such as reported by Neidhardt et al.,²⁰ and Harvey et al.⁵⁹

Associated content

Supporting Information

Additional material includes additional descriptions, Tables and Figures related to various permutations of the main 4 model variants. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/esxxxxx. Financial support was provided by an Australian Postgraduate Award, the National Centre for Groundwater Research and Training (NCGRT) and CSIRO Land and Water.

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Author Contributions

J.R. developed and calibrated the model variants under the supervision of H.P., J.A.D. and A.S. J.C., M.B. and S.F. provided input on various aspects of the conceptual models. All authors contributed to the writing of the paper.

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Literature Cited

(1) Tufano, K. J.; Fendorf, S. Confounding impacts of iron reduction on arsenic retention. *Environ. Sci. Technol.* **2008**, *42*, 4777-4783.

(2) Smedley, P. L.; Kinniburgh, D. G. A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* **2002**, *17*, 517-568.

(3) Mukherjee, S.; Roy, M.; Dey, S.; Bhattacharya, R. K. A mechanistic approach for modulation of arsenic toxicity in human lymphocytes by curcumin, an active constituent of medicinal herb *Curcuma longa* Linn. *J Clin Biochem Nutr* **2007**, *41*, 32-42.

(4) McArthur, J. M.; Banerjee, 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. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Applied Geochemistry* **2004**, *19*, 1255-1293.

(5) Fendorf, S.; Michael, H. A.; van Geen, A. Spatial and temporal variations of groundwater arsenic in South and Southeast Asia. *Science* **2010**, *328*, 1123-1127.

(6) Postma, D.; Larsen, F.; Minh Hue, N. T.; Duc, M. T.; Viet, P. H.; Nhan, P. Q.; Jessen, S. Arsenic in groundwater of the Red River floodplain, Vietnam: Controlling geochemical processes and reactive transport modeling. *Geochimica et Cosmochimica Acta* **2007**, *71*, 5054-5071.

(7) Berg, M.; Trang, P. T. K.; Stengel, C.; Buschmann, J.; Viet, P. H.; Van Dan, N.; Giger, W.; Stuben, D. 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. *Chemical Geology* **2008**, *249*, 91-112.

(8) Biswas, A.; Nath, B.; Bhattacharya, P.; Halder, D.; Kundu, A. K.; Mandal, U.; Mukherjee, A.; Chatterjee, D.; Morth, C. M.; Jacks, G. Hydrogeochemical contrast between brown and

- grey sand aquifers in shallow depth of Bengal Basin: consequences for sustainable drinking water supply. *The Science of the total environment* **2012**, *431*, 402-412.
- (9) Nickson, R. T.; McArthur, J. M.; Ravenscroft, P.; Burgess, W. G.; Ahmed, K. M. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Applied Geochemistry* **2000**, *15*, 403-413.
- (10) Polizzotto, M. L.; Kocar, B. D.; Benner, S. G.; Sampson, M.; Fendorf, S. Near-surface wetland sediments as a source of arsenic release to ground water in Asia. *Nature* **2008**, *454*, 505-505.
- (11) Anawar, H. M.; Akai, J.; Sakugawa, H. Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in groundwater. *Chemosphere* **2004**, *54*, 753-762.
- (12) Appelo, C. A. J.; Van der Weiden, M. J. J.; Tournassat, C.; Charlet, L. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ. Sci. Technol.* **2002**, *36*, 3096-3103.
- (13) Gao, X. B.; Wang, Y. X.; Hu, Q. H.; Su, C. L. Effects of anion competitive adsorption on arsenic enrichment in groundwater. *J Environ Sci Heal A* **2011**, *46*, 471-479.
- (14) Stollenwerk, K. G.; Breit, G. N.; Welch, A. H.; Yount, J. C.; Whitney, J. W.; Foster, A. L.; Uddin, M. N.; Majumder, R. K.; Ahmed, N. Arsenic attenuation by oxidized aquifer sediments in Bangladesh. *Science of the Total Environment* **2007**, *379*, 133-150.
- (15) Tufano, K. J.; Reyes, C.; Saltikov, C. W.; Fendorf, S. Reductive Processes Controlling Arsenic Retention: Revealing the Relative Importance of Iron and Arsenic Reduction. *Environ. Sci. Technol.* **2008**, *42*, 8283-8289.
- (16) Nguyen Thi Hoa Mai, D. P., Pham Thi Kim Trang, Søren Jessen, Pham Hung Viet, Flemming Larsen. Adsorption and desorption of arsenic to aquifer sediment on the Red-River floodplain at Nam Du Vietnam. *Geochimica et Cosmochimica Acta* **2014**, *142*, 587-600.
- (17) Dixit, S.; Hering, J. G. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.* **2003**, *37*, 4182-4189.
- (18) Manning, B. A.; Fendorf, S. E.; Goldberg, S. Surface structures and stability of arsenic(III) on goethite: Spectroscopic evidence for inner-sphere complexes. *Environ. Sci. Technol.* **1998**, *32*, 2383-2388.
- (19) Raven, K. P.; Jain, A.; Loeppert, R. H. Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. *Environmental science & technology* **1998**, *32*, 344-349.
- (20) Neidhardt, H.; Berner, Z. A.; Freikowski, D.; Biswas, A.; Majumder, S.; Winter, J.; Gallert, C.; Chatterjee, D.; Norra, S. Organic carbon induced mobilization of iron and manganese in a West Bengal aquifer and the muted response of groundwater arsenic concentrations. *Chemical Geology* **2014**, *367*, 51-62.
- (21) Hansel, C. M.; Benner, S. G.; Neiss, J.; Dohnalkova, A.; Kukkadapu, R. K.; Fendorf, S. Secondary mineralization pathways induced by dissimilatory iron reduction of ferrihydrite under advective flow. *Geochimica Et Cosmochimica Acta* **2003**, *67*, 2977-2992.
- (22) Jonsson, J.; Sherman, D. M. Sorption of As(III) and As(V) to siderite, green rust (fougerite) and magnetite: Implications for arsenic release in anoxic groundwaters. *Chemical Geology* **2008**, *255*, 173-181.
- (23) Herbel, M.; Fendorf, S. Biogeochemical processes controlling the speciation and transport of arsenic within iron coated sands. *Chemical Geology* **2006**, *228*, 16-32.
- (24) Kocar, B. D.; Herbel, M. J.; Tufano, K. J.; Fendorf, S. Contrasting effects of dissimilatory iron(III) and arsenic(V) reduction on arsenic retention and transport. *Environmental science & technology* **2006**, *40*, 6715-6721.
- (25) Yang, L.; Steefel, C. I.; Marcus, M. A.; Bargar, J. R. Kinetics of Fe(II)-Catalyzed Transformation of 6-line Ferrihydrite under Anaerobic Flow Conditions. *Environ. Sci. Technol.* **2010**, *44*, 5469-5475.

- (26) Tufano, K. J.; Benner, S. G.; Mayer, K. U.; Marcus, M. A.; Nico, P. S.; Fendorf, S. Aggregate-Scale Heterogeneity in Iron (Hydr)oxide Reductive Transformations. *Vadose Zone J* **2009**, *8*, 1004-1012.
- (27) Benner, S. G.; Hansel, C. M.; Wielinga, B. W.; Barber, T. M.; Fendorf, S. Reductive dissolution and biomineralization of iron hydroxide under dynamic flow conditions. *Environ. Sci. Technol.* **2002**, *36*, 1705-1711.
- (28) Prommer, H.; Davis, G. B.; Barry, D. A. Geochemical changes during biodegradation of petroleum hydrocarbons: field investigations and biogeochemical modelling. *Org Geochem* **1999**, *30*, 423-435.
- (29) Coello, C. A. C.; Pulido, G. T.; Lechuga, M. S. Handling multiple objectives with particle swarm optimization. *Ieee T Evolut Comput* **2004**, *8*, 256-279.
- (30) Eberhart, R., and J. Kennedy A new optimizer using particle swarm theory. *Micro Machine and Human Science, Sixth International Symposium on* **1995**, 39-43.
- (31) Kennedy, J. R., R. Eberhart, and Y. Shi. Swarm Intelligence. *Morgan Kaufman Publishers Inc., San Francisco, CA.* **2001**.
- (32) Parkhurst, D. L.; Appelo, C. A. J.; Geological Survey (U.S.): *User's guide to PHREEQC (version 2) a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*; U.S. Geological Survey : Earth Science Information Center, Open-File Reports Section distributor, 1999.
- (33) Harbaugh, A. W.; Geological Survey (U.S.): *MODFLOW-2000, the U.S. Geological Survey modular ground-water model user guide to modularization concepts and the ground-water flow process*; U.S. Geological Survey ; Branch of Information Services distributor: Reston, VA, Denver, CO, 2000.
- (34) Prommer, H.; Barry, D. A.; Zheng, C. MODFLOW/MT3DMS-based reactive multicomponent transport modeling. *Ground Water* **2003**, *41*, 247-257.
- (35) Zheng, C. W., P.P. MT3DMS: A Modular Three-Dimensional Multispecies Transport Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems; Documentation and User's Guide. **1999**.
- (36) Welter, D. E., White, J.T., Hunt, R.J., and Doherty, J.E.: *Approaches in highly parameterized inversion— PEST++ Version 3, a Parameter ESTimation and uncertainty analysis software suite optimized for large environmental models*; U.S. Geological Survey Techniques and Methods, book 7, 2015.
- (37) Wallis, I.; Prommer, H.; Simmons, C. T.; Post, V.; Stuyfzand, P. J. Evaluation of Conceptual and Numerical Models for Arsenic Mobilization and Attenuation during Managed Aquifer Recharge. *Environmental science & technology* **2010**, *44*, 5035-5041.
- (38) Dzombak, D. A. M., Francois M.M.: *Surface Complexation Modelling*; Wiley: United States of America, 1990.
- (39) Liu, F.; De Cristofaro, A.; Violante, A. Effect of pH, phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite. *Soil Sci* **2001**, *166*, 197-208.
- (40) Zhao, H. S.; Stanforth, R. Competitive adsorption of phosphate and arsenate on goethite. *Environ. Sci. Technol.* **2001**, *35*, 4753-4757.
- (41) Michel, F. M.; Ehm, L.; Antao, S. M.; Lee, P. L.; Chupas, P. J.; Liu, G.; Strongin, D. R.; Schoonen, M. A. A.; Phillips, B. L.; Parise, J. B. The structure of ferrihydrite, a nanocrystalline material. *Science* **2007**, *316*, 1726-1729.
- (42) Hansel, C. M.; Benner, S. G.; Fendorf, S. Competing Fe(II)-induced mineralization pathways of ferrihydrite. *Environ. Sci. Technol.* **2005**, *39*, 7147-7153.
- (43) Hansel, C. M. Bacterial and Geochemical controls on the reductive dissolution and secondary mineralization of iron (hydr) oxides. Ph.D. Dissertation, Stanford University. 2004.
- (44) Kocar, B. D.; Fendorf, S. Thermodynamic Constraints on Reductive Reactions Influencing the Biogeochemistry of Arsenic in Soils and Sediments. *Environmental science & technology* **2009**, *43*, 4871-4877.

- (45) Wang, Y. H.; Morin, G.; Ona-Nguema, G.; Menguy, N.; Juillot, F.; Aubry, E.; Guyot, F.; Calas, G.; Brown, G. E. Arsenite sorption at the magnetite-water interface during aqueous precipitation of magnetite: EXAFS evidence for a new arsenite surface complex. *Geochimica Et Cosmochimica Acta* **2008**, *72*, 2573-2586.
- (46) Ball, J. W.; Nordstrom, D.K.; Geological Survey (U.S.). User's manual for Wateq4f, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. **1991**.
- (47) Bhandari, N.; Reeder, R. J.; Strongin, D. R. Photoinduced Oxidation of Arsenite to Arsenate on Ferrihydrite. *Environ. Sci. Technol.* **2011**, *45*, 2783-2789.
- (48) Amstetter, K.; Borch, T.; Larese-Casanova, P.; Kappler, A. Redox Transformation of Arsenic by Fe(II)-Activated Goethite (α -FeOOH). *Environ. Sci. Technol.* **2010**, *44*, 102-108.
- (49) Levenberg, K. A. A method for the solution of certain non-linear problems in least squares. *Quarterly Journal of Applied Mathematics* **1944**, *11*, 164-168.
- (50) Doherty, J. E. PEST-Model-Independent Parameter Estimation: User's Manual, 5th ed. **2010**.
- (51) Marquardt, D. W. An algorithm for the least-squares estimation of nonlinear parameters. *SIAM* **1963**, *11*, 431-441.
- (52) Pierce, M. L.; Moore, C. B. Adsorption of Arsenite and Arsenate on Amorphous Iron Hydroxide. *Water research* **1982**, *16*, 1247-1253.
- (53) Borch, T.; Masue, Y.; Kukkadapu, R. K.; Fendorf, S. Phosphate imposed limitations on biological reduction and alteration of ferrihydrite. *Environmental science & technology* **2007**, *41*, 166-172.
- (54) Paige, C. R.; Snodgrass, W. J.; Nicholson, R. V.; Scharer, J. M. An arsenate effect on ferrihydrite dissolution kinetics under acidic oxic conditions. *Water research* **1997**, *31*, 2370-2382.
- (55) Zachara, J. M.; Kukkadapu, R. K.; Fredrickson, J. K.; Gorby, Y. A.; Smith, S. C. Biomineralization of poorly crystalline Fe(III) oxides by dissimilatory metal reducing bacteria (DMRB). *Geomicrobiol J* **2002**, *19*, 179-207.
- (56) Roden, E. E.; Zachara, J. M. Microbial reduction of crystalline iron(III) oxides: Influence of oxide surface area and potential for cell growth. *Environ. Sci. Technol.* **1996**, *30*, 1618-1628.
- (57) Cornell, R. M.; Schwertmann, U.: The Iron Oxides. Structure, Properties, Reactions, Occurrences and Uses. **1996**.
- (58) Coker, V. S.; Gault, A. G.; Pearce, C. I.; van der Laan, G.; Telling, N. D.; Charnock, J. M.; Polya, D. A.; Lloyd, J. R. XAS and XMCD evidence for species-dependent partitioning of arsenic during microbial reduction of ferrihydrite to magnetite. *Environmental science & technology* **2006**, *40*, 7745-7750.
- (59) Harvey, C. F.; Swartz, C. H.; Badruzzaman, A. B.; Keon-Blute, N.; Yu, W.; Ali, M. A.; Jay, J.; Beckie, R.; Niedan, V.; Brabander, D.; Oates, P. M.; Ashfaq, K. N.; Islam, S.; Hemond, H. F.; Ahmed, M. F. Arsenic mobility and groundwater extraction in Bangladesh. *Science* **2002**, *298*, 1602-1606.

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Table 1: Overview of the most important model variants employed to test arsenic mobilisation and attenuation in a column study¹. All simulation include arsenic desorption by chemical disequilibrium during pore water replacement, arsenic release during reductive dissolution of iron, and adsorption of arsenic onto magnetite.

Model variant	Considered arsenic attenuation processes
S1	As(III) sorption to ferrihydrite and magnetite. No As redox transformations.
S2	S1 + As(III) incorporation with magnetite. No As redox transformations.
S3	S1 + (partial) As(III) oxidation.
S4a	S1, S2, S3 + As(III) oxidation set at 25%.
S4b	S1, S2, S3 + As(III) oxidation set at 10%.

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Table 2: Model parameters estimated by PEST/PSO.

Parameter	Model Variant						Lower bound	Upper bound
	S1	S2	S3	S4a	S4b			
Initial concentration of aqueous As(III)	1.3E-05	1.3E-05	1.6E-06	3.2E-06	3.45E-06	1.00E-06	1.00E-05	
Initial concentration of aqueous As(V)	0	0	1.5E-05	1.1E-05	1.13E-05	0.00E+00	5.00E-05	
Sorption site density of weak sites (ferrihydrite)	0.1	0.1	0.12	0.135	0.10	0.05 ^c	0.31 ^a	
Sorption site density of strong sites (ferrihydrite)	0.0025	0.0025	0.005	0.0026	0.005	N/A	N/A	
Sorption site density of weak sites (magnetite)	3.1	0.021	0.027	0.021	0.03	0.01 ^a	0.04 ^a	
Sorption site density of strong sites (magnetite)	0.008	0.0005	0.0007	0.00052	0.00068	N/A	N/A	
Arsenate and Arsenite Surface Complexation Constants for Ferrihydrite								
Hfo_wOH+ H3AsO3 = Hfo_wH2AsO3 +	5.91	5.56	5.6	5.58	5.51	4.02 ^a	5.56 ^b	
Hfo_wOH+AsO4-3+3H+= Hfo_wH2AsO4 + H2O	NA	NA	29.31	30	30.5	24.18 ^b	34.44 ^b	
Hfo_wOH+AsO4-3+2H+ = Hfo_wHAsO4- + H2O	NA	NA	23.9	23	23.18	23.18 ^b	24.43 ^a	
Hfo_wOH+AsO4-3=Hfo_wAsO4-2	NA	NA	8.5	6.95	5.28	4.69 ^a	11.48 ^b	
Arsenate and Arsenate Surface Complexation Constants for Magnetite								
Mag_wOH+ AsO3 = Mag_wH2AsO3 + H2O	5.61	5.61	5.6	5.23	6	0 ^a	7.67 ^a	
Mag_wOH+AsO4-3+3H+= Mag_wH2AsO4 + H2O	NA	NA	29.31	31.8	29.2	20	40	
Mag_wOH+AsO4-3+2H+ = Mag_wHAsO4- + H2O	NA	NA	29.31	26	23.18	19	29	
Mag_wOH+AsO4-3=Mag_wOHAsO4 ⁻³	NA	NA	8.5	10.2	5.65	5	13	
Kinetic Reaction Rate Constants								
Magnetite precipitation	5.00E-06	8.0E-04	2.5E-04	6.4E-05	5.1E-05	5.0E-05	5.00E-03	
C_m (Eqn. 3)	0.21	0.229	0.22	0.217	0.21	0.20	0.25	
As inc. into magnetite (As:Fe molar ratio)	NA	0.9	NA	0.34	0.35	5.0E-02	1.0E+00	
As:Fe molar ratio from above	NA	1:1.7	NA	1:4.5	1:3.1	NA	NA	
α (Eqn. 5)	NA	NA	9.8E-09	4.70E-09	6.0E-09	3.0E-09	6.00E-09	
Ferrihydrite dissolution	1.10E-08	1.10E-08	1.10E-08	1.07E-08	1.01E-08	1.00E+09	5.00E-08	

Hfo_wOH and Mag_wOH represent weak sorption onto ferrihydrite and magnetite respectively. Identical surface complexation constants were used for strong sorption sites onto ferrihydrite and magnetite. Concentration units mol.L⁻¹. Surface complexation constants are log K's. All other constants are unitless. ^aReference¹⁷. ^bReference³⁸. ^cReference⁵².

Figure 1: Simulation (*S4b*) and experimental results for arsenic and ferrous iron for four columns amended with varying lactate concentrations. Symbols represent observed concentrations for the abiotic (red triangle), 7.7mM (blue circle), 0.8mM (inverted black triangle), and 0.08mM (green square) column experiments from Tufano and Fendorf¹ respectively. Solid lines represent the calibrated model.

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Figure 2: *S4b* simulated column profiles for 7.7mM lactate amended column (flow from left to right).

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Row 1: Aqueous ferrous iron concentrations. Row 2 and 3 are major sorbed ions onto ferrihydrite and

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magnetite respectively; green is hydroxyl group, red is total arsenic, and blue is ferrous iron. Row 4:

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Arsenic incorporated into transforming magnetite.

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Figure 3: *S4b* simulation results at midpoint along column. Experimental results were taken from terminated columns. Top panel: Magnetite precipitation rate (solid lines) and ferrihydrite dissolution rate (dashed lines) for each of the lactate amended models. Middle panel: Simulated aqueous ferrous iron concentrations at column effluent end. Bottom panel: Simulation (solid line) and experimental results (symbol) of the iron transformation from ferrihydrite (in blue) to magnetite (in black) for each lactate amended model.

Figure 4: Simulated (dashed and solid lines, model variant *S1*) and experimental results (symbols) at the column effluent end: Simulation results with just As(III) for 7.7mM lactate and abiotic columns. The black solid line represents As(III) with a sorption site density of magnetite approximately 120 times of that reported by Dixit and Hering.¹⁷

Add lactate

Environmental Science & Technology

Fe (II)

- produced via reductive dissolution of iron
- re-sorbs onto ferrihydrite and magnetite
- induced magnetite precipitation

As(V) $\rightarrow$ As(III)
(As(V) possibly initially present)

As(V)

As(III)

As(III)

As(V)

As(III)

As(III)

Ferrihydrite

As(III)

- desorbs into groundwater
- partially re-sorbs onto magnetite and ferrihydrite
- incorporates into magnetite structure during transformation

ACS Paragon Plus Environment

Magnetite

As(III)

As(III) As(III)