**Quantifying reactive transport processes governing arsenic mobility in a Bengal
Delta aquifer**

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23 TOC Abstract

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25

26 **Abstract**

27 Over the last few decades, significant progress has been made to characterize the extent, severity, and
28 underlying geochemical processes of groundwater arsenic (As) pollution in S/SE Asia. However,
29 comparably little effort has been made to merge the findings into frameworks that allow for a process-
30 based quantitative analysis of observed As behavior and for predictions of its long-term fate. This study
31 developed field-scale numerical modeling approaches to represent the hydrochemical processes
32 associated with an *in situ* field injection of reactive organic carbon, including the reductive dissolution
33 and transformation of ferric iron (Fe) oxides and the concomitant release of sorbed As. We employed data
34 from a sucrose injection experiment in the Bengal Delta Plain to guide our model development and to
35 constrain the model parameterization. Our modeling results illustrate that the temporary pH decrease
36 associated with the sucrose transformation and mineralization caused pronounced, temporary shifts in the
37 As partitioning between aqueous and sorbed phases. The results also suggest that while the reductive
38 dissolution of Fe(III) oxides reduced the number of sorption sites, a significant fraction of the released As
39 was rapidly scavenged through co-precipitation with neo-formed magnetite. These secondary reactions
40 can explain the disparity between the observed Fe and As behavior.

41

42 **Keywords:** arsenic, reactive transport, iron mineral transformations, surface complexation, secondary
43 geochemical reactions

44

45 Introduction

46 Currently, more than 100 million people in S/SE Asia are exposed to arsenic (As) contaminated
47 groundwater above the WHO drinking water limit of $10 \mu\text{g L}^{-1}$.¹ Arsenic occurs naturally in sediments,
48 particularly in low-lying flood plain type environments with most of the noteworthy occurrences in parts
49 of Argentina, Bangladesh, Chile, China, Hungary, India, Mexico, Romania, Taiwan, and Vietnam.^{1, 2}
50 Understanding the coupled geochemical and hydrological processes that control As mobility is vital for
51 minimizing health impacts through the development of suitable mitigation strategies. Many of the major
52 field studies that were performed over the last decade suggest that the reductive dissolution of ferric iron
53 (Fe) oxides by reactive organic carbon sources is the primary process to cause As mobilization.³⁻¹¹ Fe(III)
54 oxides refer to ferric oxides, hydroxide and oxyhydroxides. During the reduction of Fe(III) oxides, sorbed
55 As is released to the groundwater while the sorption sites that host As become eliminated. Many of these
56 studies have demonstrated a relatively strong correlation between elevated groundwater As and Fe^{2+}
57 concentrations to persist within typical reducing environments.³⁻¹⁰ However, for example, Horneman et
58 al.¹² found a significant scatter in the relationship between groundwater Fe^{2+} and As concentrations in
59 their studies of a Bangladesh aquifer.

60
61 Arsenic release associated with reductive dissolution of Fe(III) oxides has been further investigated in
62 controlled laboratory batch¹³⁻¹⁵ and column studies.¹⁶⁻¹⁹ Many of these experiments also show a rather
63 poor correlation between dissolved Fe^{2+} and As. For example, Islam et al.¹³ observed a rapid increase of
64 Fe^{2+} concentrations upon the addition of acetate during a batch experiment, whilst As concentrations did
65 not increase until more than 10 days later. Furthermore, a number of flow-through column studies
66 demonstrated initially decreasing As concentrations in the effluent in response to the addition of lactate.¹⁷⁻
67 ¹⁹ The observed decrease could be attributed to the occurrence of Fe mineral transformations,²⁰⁻²² during
68 which the released As was partially captured on neo-formed sorption sites, or by co-precipitation. For
69 example, Jönsson and Sherman²³ found that both As(III) and As(V) could adsorb on the surface of
70 magnetite; Wang et al.¹⁵ showed via extended x-ray absorption fine-structure (EXAFS) spectroscopy and

some other complementary analyses that As(III) can become sequestered via surface adsorption, and by surface precipitation reactions during magnetite precipitation. In addition, Jönsson and Sherman²³ and Guo et al.²⁴ initiated batch adsorption experiments and confirmed that siderite is also effective at removing both As(V) and As(III) from solution.

In many areas of contaminant hydrology, controlled field experiments have played an important role in attempting to bridge the gap between laboratory-scale insights and field observations. However, to our knowledge, only a small number of *in situ* field experiments have been performed in which As mobilization was intentionally induced by a controlled injection of reactive organic compounds that stimulate microbial reduction. The first of these experiments was performed by Harvey et al.²⁵ in a Bangladesh aquifer. They observed groundwater As concentrations to quickly increase after the controlled injection of 8000 L of low-As water amended with 300 mg L⁻¹ molasses. Similarly As mobilization was observed by Saunders et al.²⁶, who injected 328 m³ of groundwater amended with a mixture of 108 mg L⁻¹ sucrose and 84 mg L⁻¹ methanol into an aquifer in Oklahoma. They observed a rapid increase of both dissolved As and Fe concentrations (As >1000 µg L⁻¹) after the injection. Recently, Neidhardt et al.²⁷ reported a field experiment that was performed in the Nadia district of West Bengal, India. They injected 1200 L of groundwater amended with up to 12 mol of sucrose at multiple wells to stimulate microbially mediated Fe reduction. They observed that dissolved Mn and Fe concentrations increased up to 750% and 3600%, respectively, while As increased only by a small amount, between 19% and 49%, compared to the initial baseline values. They attributed the disparity between the increases in Fe and As concentrations to the possibility that As was sorbing to the remaining Fe(III) minerals and/or to newly formed Fe(II) and mixed Fe(II/III) minerals.

Despite the enormous amount of experimental research that has been devoted to developing a qualitative understanding of the processes controlling As mobility, the capacity to quantify the processes in numerical models is still largely lacking, and with only a few exceptions,^{9, 28, 29} field-scale modeling of As mobility

has relied on highly simplified assumptions, such as the partition coefficient (K_d) adsorption model.^{25, 30,}
³¹ To date, only a handful of numerical modeling studies have addressed the linkage between As mobility
and Fe reduction. One of these studies was reported by Postma et al.⁹, who used a one-dimensional
reactive transport model to identify and quantify the geochemical processes controlling As mobility.
Employing the Dzombak and Morel's³² surface complexation model, their simulations agreed well with
the data they collected from a young Holocene aquifer at Dan Phuong, Vietnam. They inferred from their
study that the main mechanism for As mobilization is the reductive dissolution of Fe(III) oxides by
sedimentary organic carbon. Kocar et al.²⁸ recently reported a reactive transport modeling study for a site
in Cambodia. They developed and calibrated a model that was subsequently used to predict the long-term
behavior of As at their site, and found that As release may continue to occur for hundreds to thousands of
years.²⁸ Most recently Rotiroti et al.²⁹ employed a one-dimensional reactive transport model to investigate
reductive dissolution of Fe(III) oxides, and showed this to be the primary mechanism for As mobilization
at their site. However, no sorption, mineral transformation or re-precipitation reactions were considered
in their study. Despite these initial efforts, there is still a substantial gap in our capability to provide a
process-based quantification of the many complex processes that affect As mobility.

Therefore, this study focuses on progressing our recently developed, laboratory-derived modeling
framework³³ by evaluating and adopting it for the quantitative interpretation of one of the few well-
documented field injection experiments.²⁷ We employed a three-dimensional model to investigate the
spatio-temporal evolution of the geochemical processes that occurred in response to a sucrose injection
event. The key processes that we investigated include (i) microbially mediated reductive dissolution of
Fe(III) oxides and Mn(IV) oxides, (ii) reductive transformations from Fe(III) oxides to other Fe minerals,
(iii) the sorption characteristics of present and potentially newly formed Fe minerals, and (iv) cation
exchange.

122 **Materials and Methods**

123 *Field Experiment*

124 The data set underpinning our modeling study was collected during a field experiment which determined
125 the effect of sucrose ($C_{12}H_{22}O_{11}$) injection on groundwater composition in the West Bengal Delta Plain,
126 India.²⁷ The site is located within a well-known As hotspot area³⁴ about 12.5 km to the east of the city of
127 Chakdah in the Nadia district of West Bengal. This data set was selected over other previously reported
128 field-injection experiments^{25, 26} due to (i) its relatively comprehensive record of injection-induced
129 hydrogeochemical changes from multiple locations, and (ii) dissolved sulfate being under detection limit
130 of the analytical method used (0.01 mM). The absence of dissolved sulfate appeared important to avoid
131 the additional complexities induced by the potential presence of thiolated As species and the potential
132 formation of Fe sulfide minerals, which represent potential As scavengers.^{26, 35} Note, that sucrose, like
133 most organic carbon sources used in controlled experiments, is much more reactive than most natural
134 organic carbon sources.

135

136 The aquifer section that was targeted by the injection experiment consists of silty fine to coarse sand and
137 was confined by a ~3 m clay-rich aquitard. Natural groundwater flow in the generally flat-relief area is
138 considered to be slow. The study site's main infrastructure consists of five groundwater wells that were
139 screened at varying depths, as illustrated in **Figure 1**. Well A was solely used for extracting groundwater.
140 Initially, wells B, C, D, and E were injected each with 30 L of groundwater sourced from well A, which
141 was amended with sucrose. Wells B and C were injected with 2 kg of sucrose and Wells D and E were
142 injected with 4 kg of sucrose. Subsequently, groundwater was pumped from well A into wells B, C, D
143 and E, respectively, for about 18 minutes at a rate of 70 L min⁻¹. Groundwater samples were collected
144 every second day for a period of two weeks. Thereafter, groundwater sampling continued every two weeks
145 for the next seven months. The full experimental details are provided by Neidhardt et al.²⁷

146

147 The groundwater at the study site prior to the start of the injection experiment was of Ca-(Mg)-HCO₃-
148 type, anoxic with both nitrate and sulfate being below the detection limits of the analytical methods used
149 (0.09 mM and 0.01 mM, respectively), and the pH was between 7.1 and 7.2. Two distinct
150 hydrogeochemical zones were identified with sharp observed concentration gradients for Cl⁻, Na⁺,
151 Ca²⁺, NH₄⁺, Mn and As located between well screens A and B. The sediment mineralogy was dominated
152 by quartz, followed by feldspars, carbonates (calcite and dolomite), mica and chlorite. As suggested by
153 sequential extraction, amorphous Fe oxides were found to be present at an average Fe concentration of
154 2.0 g kg⁻¹ (36 mmol kg⁻¹, extracted with 1 M HCl and oxalate in dark at room temperature) while 1.5 g
155 kg⁻¹ of more crystalline Fe oxides were identified (27 mmol kg⁻¹, extracted with dithionite-citrate at 85
156 °C). Note that sediment Fe mineralogy (reactivity) suggested in respective sequential extraction steps vary
157 for the depth intervals, values given here for Fe concentrations therefore represent averages for the
158 investigated aquifer. Controlled by the (slow) decomposition of sedimentary and dissolved organic
159 carbon, the aquifer provided a geochemically reducing environment, and >90% of the dissolved As in the
160 groundwater prevailed as As(III). The aquifer was characterized by a sediment As concentration of 3.17
161 ± 0.81 mg kg⁻¹ (42.3 ± 10.8 μmol kg⁻¹, based on microwave-assisted acid digestion of 63 sediment
162 samples), groundwater As concentrations ranging from 0.62 μM in extraction well A to 2.0 μM, 1.7 μM
163 and 1.6 μM, respectively, in wells B, C and D, and was depleted in sedimentary organic matter (SOM)
164 and dissolved organic carbon (DOC).

165

166 *Numerical modeling*

167 The hydrogeochemical site characterization and the hydrochemical data collected during the injection
168 experiment formed the basis of an initial conceptual model for groundwater flow, solute transport, and
169 biogeochemical reaction processes. The conceptual model was subsequently translated into a three-
170 dimensional numerical flow and reactive transport model and, when constrained by field observations,
171 successively improved. MODFLOW³⁶ and PHT3D,³⁷ were used as simulators for flow and reactive
172 transport processes, respectively.³⁸

173

174 ***Flow and conservative transport model***

175 Initially, a three-dimensional, transient flow model spanning 16 m wide, 40 m long and 40 m deep was
176 constructed consisting of 16 rows, 40 columns and 23 layers. The boundaries were sufficiently far from
177 the extraction/injection wells to have little impact on flow and solute transport behaviour. The
178 discretization of the rows and columns were 1 m each. In the vertical direction, layers 3 to 22 were
179 discretized into thin layers of less than 1 m thickness, as injection and extraction wells were located within
180 these layers, whilst remaining layers were significantly thicker. Longitudinal dispersivity, lateral
181 transverse dispersivity and vertical transverse dispersivity were set at 0.2 m, 0.02 m and 0.002 m,
182 respectively. The total simulation time was subdivided into six stress periods with the first stress period
183 representing ambient, pre-injection conditions. The second stress period defined the gravity-fed sucrose
184 injection into each of the wells. The subsequent stress periods of about 18 minutes each represented the
185 period during which groundwater was extracted from well A and injected into wells B, C, and D,
186 respectively. Well E was ignored as the observed Cl^- data did not show any clear trends and therefore the
187 data from this well could not be considered for the development and calibration of the reactive transport
188 model.

189

190 The final stress period of 145 days represented the post-injection period, during which the original flow
191 regime was re-established. No dedicated conservative tracer was amended during the injection
192 experiment. However, Cl^- concentrations in the groundwater extracted from well A were significantly
193 higher (0.22 mM) compared to the background concentrations (0.07 mM) in the zones where the re-
194 injection took place. The Cl^- concentration differences could therefore be used to calibrate the flow and
195 nonreactive transport model.

196

Conceptual model of biogeochemical processes and reaction network implementation

Our conceptual hydrochemical model of the field injection experiment assumes that in the absence of other, more favorable electron acceptors, the injection of sucrose induced (with little to no lag-time) a kinetically controlled reduction of the bioavailable Mn(IV) oxides and Fe(III) oxides. It is assumed that the sucrose injection was the dominant driver for redox processes, and that sedimentary and naturally prevailing dissolved organic carbon had a much lower reactivity compared to sucrose and thus was not considered in the simulations. Corresponding to the sequential extraction results, two types of Fe(III) oxides were implemented into the reaction network to represent easily reducible and non-easily reducible Fe(III) oxide fractions, respectively. The fraction of easily reducible Fe(III) oxides in the sediments might include ferrihydrite, lepidocrocite and nano-goethite, all susceptible to microbial Fe reduction, whereas non-easily reducible Fe(III) oxides might include more crystalline goethite and hematite that are relatively stable. Similar to our previous, related work³³ we employ a partial equilibrium approach to represent the transformations of the organic compounds in our reaction network implementation.

Sucrose/glucose biotransformation

While sucrose was injected in the field experiment, the enzymatic hydrolysis of sucrose (Eqn. 1) often occurs very rapidly³⁹ and was therefore not explicitly modeled.

Instead, the injection of an equivalent amount of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) was simulated. Glucose degradation was modeled as a transformation to acetate, as considerable amounts of acetate were formed during the experiment.²⁷

Acetate was then assumed to completely mineralize:

Both degradation reactions were modeled as first-order reactions:

$$R_{glu/ace} = k_{1,glu/ace} C_{gluc/ace} \quad (4)$$

223 where $k_{1,glu/ace}$ is a rate constant and $C_{gluc/ace}$ refers to either glucose or acetate concentration.

224

225 ***Reductive dissolution of iron and manganese oxides***

226 Ferrihydrite and pyrolusite were the two main electron acceptors that were considered in the simulations,
227 both representing the bio-available and reactive pool of oxidized Fe and Mn minerals, respectively, i.e.,

229 and

231 Ferrihydrite was used in the numerical models as the proxy for all easily reducible Fe(III) oxides, similar
232 to Postma et al.⁴⁰ in which goethite (FeOOH) was used as the “model mineral” to represent Fe(III) oxides
233 in Holocene sediments for their long-term reactive transport simulations. Note that ferrihydrite is
234 represented as Fe(OH)₃ here, both for simplicity and to represent natural variation, while a stoichiometry
235 of Fe₁₀O₁₄(OH)₂·0.74H₂O has been suggested for ferrihydrite in its pure form.⁴¹ Both reactions were
236 modeled through a partial equilibrium approach, as proposed by Postma and Jakobsen.⁴²

237

238 ***Reductive transformation to magnetite***

239 In addition to being reductively dissolved to Fe²⁺, easily reducible Fe(III) oxide, again with ferrihydrite
240 as proxy, could also be reductively transformed to some other Fe minerals including magnetite:

242 Iron mineral transformations affect As mobility through the loss of existing sites on Fe(III) oxides and the
243 generation of new sorption sites on the neo-formed minerals. However, perhaps more importantly,
244 dissolved As that is released during microbial reduction of the Fe(III) oxide phases may be captured within
245 the structural formation of, and/or as surface precipitates on, magnetite.^{15, 19, 43-45} Here we adopt and test
246 an approach that we successfully applied at the laboratory-scale to simulate magnetite formation and its
247 impact on As mobility.³³ The employed rate expression was originally proposed by Tufano et al.²² but

modified in Rawson et al.³³ to consider the limitation of available surface sites on easily reducible Fe(III) oxides.⁴⁶

$$R_{magn-pptn} = -k_{magn-pptn} \max \left(0, \left[1 - \frac{1}{SR_{magn}} \right] \right) \left(\frac{[Fe^{2+}]}{K_{magn-pptn}^{thres(Fe^{2+})} + [Fe^{2+}]} \right)^x \left(\frac{[ER] - C_m}{[ER]} \right) \quad (8)$$

where $k_{magn-pptn}$ is the effective rate coefficient, determined through model calibration, SR_{magn} is the saturation ratio of magnetite, $K_{magn-pptn}^{thres(Fe^{2+})}$ is a threshold term describing the aqueous Fe^{2+} concentration required for transformation of the easily reducible Fe(III) oxides to magnetite, which according to Tufano et al.²² requires an exponential term (x) set at 3, $[ER]$ is the concentration of easily reducible Fe(III) oxides and C_m is the concentration at which magnetite precipitation effectively stalls. Based on several controlled laboratory studies^{21, 22, 47}, the threshold value of 2×10^{-4} mol L⁻¹ was used as an initial estimate for $K_{magn-pptn}^{thres(Fe^{2+})}$, but was allowed to deviate slightly during the model calibration process.

Arsenite co-precipitation with magnetite

Arsenic immobilization with magnetite was considered following several studies that observed decreasing aqueous As concentrations in conjunction with Fe mineral transformations.^{15, 17, 44, 48} For example, Wang et al.¹⁵ identified As(III) amorphous surface precipitates with the freshly precipitated magnetite, which contributed to lowering the aqueous As(III) concentrations. For the present study, we adopted the approach proposed in Rawson et al.³³, in which the rate of As removal by magnetite is stoichiometrically linked with the rate of magnetite formation. The stoichiometry of the (As substitution and/or surface precipitation) reaction was assumed to be:

The molar ratio of As:Fe was determined through the model calibration process, through the parameter $Fe_3O_4As_2O_3(s)$ fraction in magnetite.

271 *Siderite precipitation*

272 While assuming that the reductive transformation of Fe(III) oxide led to magnetite formation, we also
 273 considered the possibility for siderite (FeCO₃) precipitation. The employed kinetic rate expression was

$$274 \quad R_{\text{siderite-pptn}} = k_{\text{sid-pptn}} (1 - SR_{\text{siderite}}) \quad (10)$$

275 where $R_{\text{siderite-pptn}}$ is the siderite precipitation rate, $k_{\text{sid-pptn}}$ is the reaction rate constant, and SR_{siderite}
 276 is the saturation ratio of siderite.

277

278 *Carbonate buffering*

279 With the acetate formation induced by the injection of sucrose, a temporary decline in pH, followed by a
 280 rapid recovery, was observed. The latter was attributed to mineral buffering by dissolution of carbonates
 281 (Eqn. 11). Given that both calcite and dolomite were found in the mineral analysis²⁷, and that Ca²⁺
 282 concentrations increased from 2.0 mM to 3.8 mM, specifically for well C, calcite dissolution was
 283 considered in the reaction network.

285 The rate expression proposed by Plummer et al.⁴⁹, as included in the standard PHREEQC database, was
 286 used to simulate calcite dissolution kinetics.

287

288 *Surface complexation and ion exchange reactions*

289 Surface sorption was assumed to occur as, (i) surface complexation reactions with reducible Fe(III) oxides
 290 and (ii) surface complexation reactions with non-easily reducible (remaining unreacted) Fe(III) oxides.

291 The electrostatic double layer model based on Dzombak and Morel's³² surface complexation reactions
 292 was employed. Dixit and Hering's⁵⁰ surface complexation reactions for As(III) sorption onto hydrous
 293 ferric oxides (HFO) were incorporated into the model. Also, surface complexation reactions for
 294 phosphate⁵¹ and carbonate⁵² were incorporated into the model to consider potential competitive sorption
 295 effects with these and other ions. Similar to Postma et al.⁹, the site density that was employed to represent
 296 the sorption sites provided by the natural Fe(III) oxides (0.013 mol and 0.002 mol weak sites per mol of

Fe for easily reducible and non-easily reducible Fe(III) oxides, respectively) was substantially reduced compared to the value that is more representative for the lab-synthesized HFO as used in the experiments of Dixit and Hering's⁵⁰ (0.2 mol weak sites per mol of HFO). Note, that the number of sorption sites for easily reducible Fe(III) oxides was stoichiometrically linked with the temporally varying mineral concentrations while the number of sorption sites associated with the non-easily reducible Fe(III) oxides was assumed to be constant. All stoichiometries of the considered surface complexation reactions are listed in Table 1. Finally, an exchanger site was implemented to account for cation exchange, with reactions:

where Cat = H⁺, Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺, Mn²⁺ and Fe²⁺. The equilibrium constants were adopted from the standard PHREEQC database and not varied during model calibration. The cation exchange capacity was determined as part of the model calibration process.

Model calibration strategy

The model parameters associated with the numerical implementation were estimated by minimizing the sum of squared residuals between model-simulated and experimentally measured concentrations for all constituents shown in Figure 2. The Gauss-Levenberg-Marquardt method was employed using the PEST software suite to further refine the model parameters.⁵³⁻⁵⁶ The parameters to be estimated in this study included a number of kinetic reaction rate constants, As surface complexation constants, surface site densities associated with specific Fe minerals, and hydrologic parameters. Observation weights were assigned based on both the magnitude and the uncertainty inherent in each observation. Calibration was conducted in parallel using the PEST++ software⁵⁷ implemented on the CSIRO Bowen Research Cloud. Parameter estimates and calibration statistics are listed in Table 1.

321 Results and Discussion

322 *Conservative transport behaviour*

323 After model calibration of the conservative transport behavior, which mostly relied on slight adjustments
324 of initially estimated hydraulic conductivities (see Table 1 for values), the model simulations provide a
325 reasonable representation of the measured Cl^- data for injection wells B, C and D. Figure 2 and Supporting
326 Information (SI) Figures SI1 and SI2 illustrate the comparison between simulated and measured
327 concentrations for the three wells, showing the rapid temporary increase of Cl^- after the sucrose injection,
328 before returning slowly back to background levels. As expected, given the vertical variations in the grain
329 size distribution, the latter occurred at different rates at different monitoring wells (wells B and C <50
330 days, well D >120 days), which also suggests slightly different natural groundwater flow velocities,
331 ranging from 1.3 to 5.1 m year⁻¹, in the respective layers in which the wells were screened.

332

333 *Carbon cycling and pH*

334 Immediately after the start of the injection, sucrose/glucose concentrations increased rapidly,
335 accompanied by an increase in alkalinity and acetate concentrations and a sharp decrease in pH (Figure
336 2). The concentration peak was followed by a more steady concentration decline over the following 10
337 days. The observed patterns were well matched by the reactive transport simulations in which a rapid
338 transformation from sucrose/glucose to acetate and a subsequent, kinetically controlled, mineralization of
339 acetate were simulated (Figure SI3). Model simulation results (Figure 2) illustrate the impact of reaction
340 processes on the injection-induced concentration changes, with comparison between (i) a purely
341 conservative (non-reactive) model, and (ii) a calibrated model in which all reactions were included. This
342 comparison (Figure 2) shows that in the absence of degradation and other reactions (i.e., conservative
343 simulation), it would have taken 30 days for the glucose-amended zone to be completely transported away
344 from well C as a result of the ambient groundwater flow. On the other hand, in the reactive simulation
345 glucose concentrations diminished quickly due to degradation, with glucose concentrations returning back
346 to zero after 12 days, in agreement with the experimental data. Furthermore, the measured alkalinity data

are well represented by the simulation results for well C (Figure 2). Similar simulation results, and a similarly good agreement with the observed data, were obtained for wells B and D (Figures SI1 and SI2).

Although in the experiment care was taken to achieve specific amounts of sucrose injected, due to some operational inconsistencies²⁷ and the high degree of sensitivity associated with these values in the model, they were allowed to vary slightly during the calibration process (Table 1). The estimated values, however, agree reasonably well with Neidhardt et al.,²⁷ including the fact that there was more sucrose injected into well B compared to wells C and D.

Reductive dissolution of iron and manganese oxides

Coinciding with the onset of the sucrose degradation, the model simulations show, in good agreement with the field data (Figure 2), a rapid increase of dissolved Mn (up to 0.33 μM in well C) and Fe concentrations (up to 0.43 mM in well C). After ~10 days, dissolved Mn and Fe concentrations started to decrease slowly back towards background concentrations at wells B and C (Figures 2 and SI1). At well D, dissolved Mn and Fe concentrations decreased much more gradually (Figure SI2). This can be attributed to slower groundwater flow velocities in the aquifer section in which well D was screened, as indicated by the conservative transport behaviour based on the measured Cl^- data. With the relatively small amount of pyrolusite being rapidly depleted the model simulations confirm that reductive dissolution of Fe(III) oxides acted as the dominant electron accepting process.

Figure 3A illustrates the importance of individual geochemical processes on the simulated dissolved Fe concentrations (more details on model variants are given in Table SI1). Besides the primary reductive dissolution reaction, cation exchange shows to have the single most important influence on the observed breakthrough behaviour by taking up a substantial fraction of the Fe that was released during the reductive dissolution. Other secondary processes that, although to a lesser extent, affect the simulated dissolved Fe concentrations include the precipitation of reduced Fe(II)-containing minerals (Figures 2 and 3A). In the

model simulations, the increase in dissolved Fe and carbonate concentrations after the sucrose injection resulted in an oversaturation/precipitation of siderite; in contrast, the simulated formation of (small quantity of) magnetite was not found to affect dissolved Fe concentrations significantly. The total amount of precipitated magnetite remained very low at $1.2 \times 10^{-6} \text{ mol L}^{-1}$ (Fe concentration: 0.1 mg kg^{-1} , $2 \text{ }\mu\text{mol kg}^{-1}$) compared to the initial concentration of easily reducible Fe(III) oxides of 0.065 mol L^{-1} (Fe concentration: 2.0 g kg^{-1} , 36 mmol kg^{-1}). As seen in Figure 2 for well C, magnetite formation occurred in the model simulations only for a brief period before stopping approximately 15 days after the start of the sucrose injection.

Arsenic mobilization

Following the sucrose injection, As concentrations at well C decreased very briefly from the background value of $1.7 \text{ }\mu\text{M}$ to a minimum of $1.2 \text{ }\mu\text{M}$ as a result of the lower As concentrations in the injected water that was sourced from well A (Figure 2). Concentrations rapidly increased thereafter to a maximum of $2.0 \text{ }\mu\text{M}$ at day 4. Overall this was a surprisingly small increase considering the strong evidence for the occurrence of reductive dissolution of Fe(III) oxides by the concomitant increase in dissolved Fe from 0.10 to 0.42 mM . The model simulation results suggest that dissolved As concentrations, after the injection, were affected by multiple simultaneous processes (Figure 3B). Several variants of the calibrated model were constructed to elucidate which processes most effectively contributed to the release and the attenuation of As. Initially, three different processes were investigated with respect to their importance for As release, i.e., (i) the impact of the temporal pH variations on the sorption equilibria, (ii) As release due to the destruction of sorption sites associated with the reductive dissolution of Fe(III) oxides, and (iii) the impact of increasing bicarbonate concentrations on the competitive desorption of As. For all variants it was found that As sorption to the non-easily reducible Fe fraction had no significant influence on simulation results.

398 Influence of pH. First, the influence of the pH variations induced by sucrose degradation was investigated
399 by (i) eliminating sucrose degradation, as well as the competitive sorption effects with bicarbonate, and
400 (ii) by triggering a similar pH drop through the addition of hydrochloric acid (HCl) to the injectant solution
401 (more details on model variants are given in Table SII). In this model variant, no reductive dissolution of
402 Fe oxides was allowed to occur. The results show that simulated As concentrations for well C increased
403 from 1.7 μM (background value) to 2.0 μM at day 8 (Figure 3B), as the pH decreased from 7.16 to 6.70.

404

405 The potential for the release of As(III) under the site-specific hydrochemical conditions is a result of the
406 decreasing sorption affinity, with decreasing pH, in the employed surface complexation model of Dixit
407 and Hering.⁵⁰ Using parameters from the calibrated model the simulated arsenite sorption edge (Figure
408 3C) suggests dissolved As(III) concentrations increase by about 0.5 μM , close to the increase simulated
409 by the reactive transport model. Due to the sorption dependency on pH, the simulated As concentrations
410 are relatively sensitive to capturing pH buffering mechanisms accurately.

411

412 Loss of sorption sites. The isolated impact of Fe(III) oxide dissolution, and its associated loss of sorption
413 capacity, was investigated by artificially fixing the pH during the entire simulation to the background pH
414 (7.16) and, as before, eliminating bicarbonate from the surface complexation model to avoid competitive
415 desorption of As by bicarbonate. In this model variant, dissolved As(III) concentrations were higher than
416 corresponding results from the simulations with a non-reactive model (i.e., all reactive processes switched
417 off), suggesting that As desorption from the loss of sorption sites could in part explain the As mobilization
418 observed in the injection experiment (Figure 3B, see “Fe reduction only” curve).

419

420 Bicarbonate competition. The impact of bicarbonate competition was investigated by adding surface
421 complexation of bicarbonate back into the above model variant. However, no significant difference was
422 found in comparison to the previous simulation (i.e., trend identical to the “Fe reduction only” curve),

demonstrating that the bicarbonate production that occurred in response to the sucrose degradation was not responsible for the field-observed As mobilization.

Overall, the model simulations illustrate that both, the temporarily decreasing pH, and the loss of surface complexation sites resulting from reductive dissolution of Fe(III) oxides were the two main contributors to the observed As mobilization. However, if applied together, this leads to an overestimation of the simulated As concentration, if not combined with a mechanism for As attenuation (Figure 3B).

Arsenic attenuation

The model simulations suggest that dissolved As was partially attenuated subsequent to its release from the Fe(III) oxide-hosted sorption sites. For example at well C, it took chloride concentrations 30 days to return to background levels after the sucrose injection, whilst dissolved As concentrations returned to background levels within approximately 10 days (Figure 2). Two different geochemical processes were investigated with respect to their ability to plausibly explain the observed As attenuation.

The first investigated possibility was that As(III) was re-sorbed to the remaining Fe minerals. However, only a minimal attenuation was observed as a result of resorption. While we recognise that As(III) sorption was not simulated by a site-specific surface complexation model (SCM), it is considered unlikely that a site-specific SCM would change the low importance of As(III) resorption fundamentally. Instead, the most significant attenuation occurred when co-precipitation of As with magnetite was assumed. In this case, specifically for well C, the simulations were able to reproduce the observed dissolved As(III) and Fe concentrations closely, and the best agreement was achieved when a As:Fe molar ratio of 1:4 was assumed ($\text{Fe}_3\text{O}_4\text{As}_2\text{O}_3(\text{s})$ fraction in magnetite was 0.387, Table 1). Previous studies suggested that such high molar ratios are unlikely to occur as a result of As(III) incorporation into the magnetite structure.⁴³ However, Wang et al. found that As(III) can form surface precipitation with magnetite, creating a thin layer with high As to Fe ratios.¹⁵

449

450 **Implications**

451 For many of the groundwater systems that are most severely affected by As pollution, the reductive
452 dissolution and transformation of Fe(III) oxides by reactive organic carbon compounds is thought to be
453 the key process to explain the presence of elevated As concentrations.³⁻¹¹ Conceptually this mechanism,
454 i.e., the successive destruction of sorption sites, provides a plausible explanation for sediment As release
455 into groundwater. However, depending on site-specific or, as in this study, *in situ* field conditions, the
456 importance of this process on controlling the fate and transport of As may vary widely. Our model-based
457 analysis of a sucrose injection experiment in West Bengal, India²⁷ illustrates that the degradation of
458 reactive organic carbon may be accompanied by a complex set of secondary geochemical reactions. In
459 the investigated case, only the model variants that incorporated a range of secondary reactions were able
460 to approximate the field observations and could thus explain the observed poor correlation between
461 increases in dissolved Fe and As concentrations. The employed reaction network which best captured the
462 field observations evolved from the conceptual model and its numerical implementation that was
463 originally developed for a well-controlled laboratory experiment where Fe mineral transformations played
464 a dominant role.^{19, 33} In comparison, the importance of Fe mineral transformations on As mobility appears
465 to be less pronounced in the present study. Possible reasons are that even with calcite buffering, temporary
466 pH change and subsequent As desorption was significant in the field experiment while the previously
467 modeled laboratory column experiment was well buffered with PIPES; and that sucrose injection occurred
468 as “pulsed” injection while the laboratory column experiment was continuously fed with a reactive
469 organic carbon source.^{27, 33} While these results are encouraging and important in terms of developing a
470 process-based model that quantifies As mobility, they should still be underpinned by additional field-scale
471 experiments that more systematically eliminate uncertainties and more rigorously document the
472 geochemical and mineralogical changes that are induced by the release of reactive organic compounds.

473

474 **Supporting Information**

475 Additional material includes a table explaining different model variants and two additional figures related
476 to field and modeling results for wells B and D. The Supporting Information is available free of charge
477 on the ACS Publications website at DOI: 10.1021/esxxxxx.

478

479 **Author Contributions**

480 J.R. developed and calibrated the numerical model variants under the supervision of H.P., A.S. and J.S.
481 while H.N. and M.B. provided guidance on conceptual model development. All authors contributed to the
482 writing of the paper.

483

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485

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490

491 **Table 1: Key model parameters employed in the calibrated model.**

Parameter	Estimated	Prior	Posterior	Uncertainty Bounds		Composite
	Parameter Value	Standard Deviation	Standard Deviation	Mean Minus Two Standard Deviations	Mean Plus Two Standard Deviations	Scaled Sensitivity
Hor. hydraulic conductivity in depth 0 – 28 m (m day^{-1})	3.12	1.00	1.98×10^{-1}	2.73	3.52	3.29×10^{-4}
Hor. hydraulic conductivity in depth 28 – 32 m (m day^{-1})	7.61×10^{-1}	5.00×10^{-1}	4.14×10^{-2}	6.78×10^{-1}	8.43×10^{-1}	4.24×10^{-4}
Porosity	3.22×10^{-1}	3.75×10^{-2}	1.45×10^{-2}	2.93×10^{-1}	3.51×10^{-1}	3.37×10^{-4}
Hydraulic head – Upstream (m)	10.59	5.00×10^{-1}	1.43×10^{-1}	10.30	10.88	2.44×10^{-3}
Hydraulic head – Remainder (m)	10.01	5.00×10^{-1}	1.59×10^{-1}	9.70	10.33	1.84×10^{-3}
Injected Amount of Sucrose (mol)						
Well B	12.72	4.95	9.55×10^{-1}	10.81	14.63	9.40×10^{-5}
Well C	8.96	4.95	7.76×10^{-1}	7.41	10.51	1.17×10^{-4}
Well D	2.76	6.11	1.56×10^{-1}	2.45	3.07	6.13×10^{-5}
Kinetic Reaction Rate Constants and Related Parameters						
Glucose degradation, $K_{l, \text{glu}}$	1.45×10^{-1}	7.50×10^{-2}	1.16×10^{-2}	1.22×10^{-1}	1.68×10^{-1}	1.24×10^{-4}
Acetate degradation, $K_{l, \text{ace}}$	3.97×10^{-8}	2.48×10^{-7}	2.15×10^{-9}	3.54×10^{-8}	4.40×10^{-8}	1.20×10^{-4}
Magnetite precipitation, $K_{\text{magn_pptn}}$	8.00×10^{-12}	1.25×10^{-3}	7.94×10^{-13}	6.41×10^{-12}	9.59×10^{-12}	3.97×10^{-4}
Threshold $K_{\text{magn_pptn}}^{\text{thres}}(\text{Fe}^{2+})$ (mol L^{-1})	1.11×10^{-4}	5.25×10^{-5}	1.43×10^{-5}	8.19×10^{-5}	1.39×10^{-4}	4.11×10^{-5}
Siderite precipitation, $K_{\text{sid_pptn}}$	2.98×10^{-11}	2.48×10^{-10}	2.24×10^{-12}	2.53×10^{-11}	3.43×10^{-11}	3.07×10^{-4}
Calcite dissolution rate constant	4.03×10^{-1}	1.13×10^{-1}	2.53×10^{-2}	3.53×10^{-1}	4.54×10^{-1}	4.12×10^{-4}
$\text{Fe}_3\text{O}_4\text{As}_2\text{O}_3(\text{s})$ fraction in magnetite	3.87×10^{-1}	1.25×10^{-1}	5.64×10^{-2}	2.74×10^{-1}	5.00×10^{-1}	8.56×10^{-5}
Exchange Species (mol L^{-1})						
X_{ex}	4.48×10^{-2}	1.23×10^{-1}	2.17×10^{-3}	4.05×10^{-2}	4.92×10^{-2}	2.02×10^{-4}
Sorption Site Densities (mol of sites per mol of Fe)						
Weak sites on easily reducible Fe(III) oxides (ER_w)	1.31×10^{-2}	2.25×10^{-2}	8.42×10^{-4}	1.15×10^{-2}	1.48×10^{-2}	6.66×10^{-4}
Weak sites on non-easily reducible Fe(III) oxides (nER_w)	2.03×10^{-3}	2.25×10^{-3}	9.36×10^{-5}	1.85×10^{-3}	2.22×10^{-3}	5.26×10^{-4}
Surface Complexation Constants (log Ks)						
$\text{ER_wOH} + \text{AsO}_3^{3-} + 3\text{H}^+ = \text{ER_wH}_2\text{AsO}_3 + \text{H}_2\text{O}$	37.65	1.13	7.25×10^{-1}	36.20	39.10	9.39×10^{-4}
$\text{ER_wOH} + \text{AsO}_3^{3-} + 2\text{H}^+ = \text{ER_wHAsO}_3^- + \text{H}_2\text{O}$	31.52	5.00×10^{-1}	2.92×10^{-1}	30.93	32.10	2.83×10^{-3}
$\text{nER_wOH} + \text{AsO}_3^{3-} + 3\text{H}^+ = \text{nER_wH}_2\text{AsO}_3 + \text{H}_2\text{O}$	37.00	6.25×10^{-1}	6.22×10^{-1}	35.76	38.24	1.08×10^{-4}
$\text{nER_wOH} + \text{AsO}_3^{3-} + 2\text{H}^+ = \text{nER_wHAsO}_3^- + \text{H}_2\text{O}$	30.27	5.00×10^{-1}	4.95×10^{-1}	29.28	31.26	2.79×10^{-4}
$\text{ER_wOH} + \text{PO}_4^{3-} + 3\text{H}^+ = \text{ER_wH}_2\text{PO}_4 + \text{H}_2\text{O}$	31.03	8.75×10^{-1}	2.33×10^{-1}	30.56	31.49	2.04×10^{-3}
$\text{ER_wOH} + \text{PO}_4^{3-} + 2\text{H}^+ = \text{ER_wHPO}_4^- + \text{H}_2\text{O}$	22.00	8.75×10^{-1}	8.20×10^{-1}	20.36	23.64	1.38×10^{-4}
$\text{ER_wOH} + \text{PO}_4^{3-} + \text{H}^+ = \text{ER_wPO}_4^{2-} + \text{H}_2\text{O}$	19.55	1.25	4.72×10^{-1}	18.61	20.50	1.14×10^{-3}
$\text{nER_wOH} + \text{PO}_4^{3-} + 3\text{H}^+ = \text{nER_wH}_2\text{PO}_4 + \text{H}_2\text{O}$	31.23	8.75×10^{-1}	7.87×10^{-1}	29.65	32.80	1.01×10^{-3}
$\text{nER_wOH} + \text{PO}_4^{3-} + 2\text{H}^+ = \text{nER_wHPO}_4^- + \text{H}_2\text{O}$	22.56	8.75×10^{-1}	8.10×10^{-1}	20.94	24.18	5.68×10^{-4}
$\text{nER_wOH} + \text{PO}_4^{3-} + \text{H}^+ = \text{nER_wPO}_4^{2-} + \text{H}_2\text{O}$	18.09	3.75×10^{-1}	3.63×10^{-1}	17.36	18.81	3.38×10^{-4}

492 Note: The initial concentration of easily reducible Fe(III) oxide was set at $6.5 \times 10^{-2} \text{ mol L}^{-1}$ (Fe: 2.0 g kg^{-1} , 36 mmol kg^{-1}), non-easily reducible Fe(III) oxide at $4.8 \times 10^{-2} \text{ mol L}^{-1}$ (Fe: 1.5 g kg^{-1} , 27 mmol kg^{-1}), pyrolusite at $8.1 \times 10^{-5} \text{ mol L}^{-1}$
493 $(\text{Mn: } 2.5 \text{ mg kg}^{-1}, 45 \text{ } \mu\text{mol kg}^{-1})$, and both siderite and magnetite at 0. These initial concentrations originated from
494 Neidhardt et al.²⁷ ER_wOH and nER_wOH represent weak sorption onto easily reducible Fe(III) oxides and non-easily
495 reducible Fe(III) oxides, respectively. The upper and lower bounds for each parameter are determined based on available
496 data in literature and expert knowledge; similar calibration ranges were used for ER_wOH and nER_wOH surface
497 complexation constants.
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Figure 1: (Right) Schematic illustration of the experimental setup at the Chakdah (West Bengal Plain field) site.²⁷ Groundwater was extracted from well A and injected into the remaining four wells. Initially, sucrose was amended to a small amount of this groundwater (from well A) and injected via gravity into the remaining wells; and, subsequently groundwater was pumped from well A and injected directly into the other wells using a pump. Well E was ignored in this study, as the observed Cl^- data did not show any clear trends and therefore the data from this well could not be considered for the development and calibration of the numerical model. (Left) Simulated aqueous concentrations of As(III), Fe, acetate and pH after 5 days for wells B, C and D; the groundwater flow direction is from the right to the left.

Figure 2: Field experimental results (symbols), calibrated reactive model results (solid lines) and non-reactive (i.e., conservative) model results (dash lines) for well C. After the short injection of sucrose/glucose concentrations, most constituents spiked. Higher Cl^- concentrations were found in well A from which groundwater was extracted. These higher Cl^- concentrations were injected into wells B, C, and D, and used to constrain groundwater flow and conservative transport. Mineral transformations from the calibrated reactive model are plotted as changes (i.e., delta) to initial conditions. Iron(III) oxide dissolution and the decrease in pH releases As whilst precipitation reactions, specifically magnetite, attenuate As via co-precipitation.

Figure 3: Figure 3AB: Field experimental results (symbols) and model simulations (solid and dash lines) illustrating (A) dissolved Fe and (B) dissolved As(III) concentrations for well C, with 6 model variants: (i) a calibrated model with all biogeochemical reactions incorporated, (ii) a non-reactive model, (iii) influence of Fe(III) oxide dissolution (with fixed pH), (iv) no Fe mineral transformations, (v) the influence of pH, and (vi) no cation exchange. More details on model variants are given in Table SII. Figure 3C: As(III) sorption edge with sorbed and aqueous As(III) concentrations with differing pH values, further illustrating the effect of pH change on As solid-solution partitioning. Most of As(III) sorption depends on the surface species ER_wHAsO₃⁻ with ER standing for easily reducible Fe(III) oxides. Sorbed As(III) concentration of ~120 μM (mass per litre water) is equal to about 1.6 mg kg⁻¹ (21 $\mu\text{mol kg}^{-1}$).

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