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Surface complexation modeling of arsenic mobilization from goethite: Interpretation of an in-situ experiment

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Highlights

- Surface complexation modeling of the As release from goethite in groundwater
- One set of SCM parameters allowed modeling the measured As concentration in 7 wells
- The CD-MUSIC model performs better than the DDL under natural hydrochemical conditions
- As desorption rate and extent non-linearly controlled by many aqueous species
- Sensitivity analysis highlighted the key controls of pH, PO_4^{3-} and Ca^{2+} on As sorption

1 **ABSTRACT**

2 Sorption has been recognized as a predominant process for the mobility and transport of
3 arsenic (As) in groundwater. However, the model-based description of the chemical and
4 physical mechanisms controlling As interaction with mineral surfaces under natural
5 hydrochemical conditions remains a formidable challenge. In this study we assess and
6 compare the ability of existing surface complexation models (SCMs), the diffuse double
7 layer model (DDL) and the charge distribution multisite complexation model (CD-
8 MUSIC), to simulate As desorption from goethite in groundwater. We consider the
9 outcomes of an in-situ experiment recently performed in an arsenic-contaminated aquifer
10 of Northern China where As-loaded goethite-coated sand was deployed in 7 monitoring
11 wells. Determination and measurements of As-surface species were carried out over a
12 time period of 80 days in all monitoring wells. Simultaneous calibration of the models
13 with the measurements in the 7 wells was performed to obtain single sets of surface
14 complexation parameters for the DDL and the CD-MUSIC models, respectively.
15 Although the general dynamic pattern of the As release at the site is captured by both
16 models, the approach based on the CD-MUSIC agrees best with the field experimental
17 data without modifications of the surface complexation database compiled from previous
18 studies on goethite. Conversely, calibration of the DDL affinity constants led to
19 substantial improvement in the agreement between model simulations and the considered
20 field dataset.

21 The model outcomes and the exploration of the sensitivity of the goethite surface
22 composition to changes in hydrochemical conditions provide insights into the
23 mechanisms controlling arsenic sorption and their different description in the DDL and

the CD-MUSIC models. Both SCMs indicate that PO_4^{3-} acts as the main competitor for As(V) sorption sites, and that Fe(II) does not have a significant effect on the As(V) release despite its strong affinity for the goethite surface. Neither SCM suggests direct binding of As(III) to goethite. However, the CD-MUSIC model predicts significant formation of a goethite-Fe(II)-As(III) complex under the mildly alkaline conditions of the groundwater at the field site and that such complex is insensitive to phosphate competition. The CD-MUSIC implementation also allows capturing the non-linear charge effects of the major ions, including Ca^{2+} and Mg^{2+} , which appear to have important implication in the mechanisms of As sorption at the field site.

1. Introduction

Arsenic (As) geogenic contamination of groundwater represents a global threat to the health of millions of people in different parts of the World (Smedley and Kinniburgh, 2002; Polizzotto et al., 2008; Bretzler et al., 2018). This severe environmental problem has been extensively studied in South East Asia as, for example, in the Mekong, Red River and Bengal Deltas (Postma et al., 2007; Jessen et al., 2012; Lowers et al., 2007; Berg et al., 2008; Biswas et al., 2014; Postma et al., 2012; Kulkarni et al., 2017). Although less extensively investigated, arsenic contamination in groundwater has also been reported in several sedimentary basins in Northern China (Guo et al., 2014; Guo et al., 2008; Rodríguez-lado et al., 2013). In regions with arsenic contaminated aquifers, the drilling of drinking water wells, the planning of groundwater pumping for irrigation (Benner and Fendorf, 2010), and the design of mitigation strategies such as in-situ remediation (Sun et al., 2018) require the assessment of arsenic spatial and temporal occurrence. Thus, it is of primary importance to understand the processes governing the

release and mobility of arsenic. Over the last decades, there has been growing understanding of the fundamental role of iron (hydr)oxides for the fate and mobility of heavy metals through co-occurring dissolution, precipitation and transformation processes resulting in the release and/or incorporation of the contaminant into the structure of iron minerals (Johannesson and Neumann, 2013; Pedersen et al., 2006; Tufano and Fendorf, 2008; Kocar et al., 2010). In particular, Fe-oxides can effectively immobilize As through sorption processes due to their large surface areas and their charged reactive surface sites that provide one of the highest sorption capacity among soil minerals (Dixit and Hering, 2003; Stachowicz et al., 2006; Gustafsson and Bhattacharya, 2007; Smedley and Kinniburgh, 2002). Goethite is of particular interest due to its stability and its abundance in the subsurface (Cornell and Schwertmann, 2003; Pedersen et al., 2006; Johannesson and Neumann, 2013). The affinity of As for iron (hydr)oxides surface sites depends on the oxidation state of As, the mineralogy of Fe-oxides, the pH and aqueous charged species competing for sorption sites (Dixit and Hering, 2003; Stachowicz et al., 2006; Stachowicz et al., 2008). The interaction between arsenic and iron (hydr)oxides is of key importance for As mobility and transport in groundwater systems.

Surface complexation models (SCMs) provide a mathematical description of the surface/solution chemistry and of the competitive and synergic effects of ions adsorption considering the influence of the chemical properties of the aqueous solution and of the solids. In particular, these models consider the chemical bonding between the mineral surface and species (i.e., complexation) and the electrostatic interactions between charged surfaces and charged species (Hayes et al., 1990; Davis and Kent, 1990; Goldberg, 1992;

70 Appelo and Postma, 2005). Surface complexation reactions databases are traditionally
71 implemented based on well-controlled laboratory experiments performed with a low
72 number of aqueous species (Hayes et al., 1990; Dixit and Hering, 2003; Dzombak and
73 Morel, 1990; Mathur and Dzombak, 2006). In contrast, model-based interpretation of As
74 sorption behavior in multi-sorbate systems remain challenging as the interactions
75 between aqueous charged species can be strong, resulting in a complex, nonlinear
76 sorption behavior (Stachowicz et al., 2008). For instance, Dixit and Hering (2006)
77 successfully modeled the sorption of As(III) and Fe(II) individually but had difficulties in
78 reproducing the observations in dual-adsorbates systems using the diffuse double layer
79 (DDL) model. Stachowicz et al. (2008) satisfactorily modeled the sorption of As, Ca^{2+} ,
80 Mg^{2+} , PO_4^{3-} and HCO_3^- in dual and triple adsorbate batch systems with the CD-MUSIC
81 model and determined a single set of surface complexation parameters from observations
82 of the individual species. These promising results, towards the implementation of SCMs
83 that can provide accurate predictions under variable hydrochemical conditions, stems
84 from the consideration of microscopic information (i.e., surface and complexes structure)
85 and electrostatic interaction between charged species at the mineral surface in the CD-
86 MUSIC model. A few studies performed evaluations of field datasets by using the
87 ferrihydrite DDL and goethite CD-MUSIC models to estimate the competitive sorption
88 processes taking place on sediments of As contaminated aquifers (Jessen et al., 2012 ,
89 Biswas et al., 2014). However, the applicability of SCMs with surface complexation
90 constants typically determined from observations on single-sorbate systems to simulate
91 sorption on pure mineral phases in groundwater aquifers involving complex
92 hydrochemistry as well as flow conditions has not been rigorously tested. Therefore,

93 studies with an intermediate level of complexity are of importance to understand the
94 complex coupling between surface and solution chemistry, electrostatic interactions and
95 mass transfer processes in groundwater systems, and to assess the ability and limitations
96 of SCMs. Such studies include controlled flow-through laboratory experiments (e.g.,
97 Tufano and Fendorf, 2008; Sharma et al., 2011; Muniruzzaman et al., 2014; Li et al.,
98 2014) as well as pilot scale field experiments (Neidhardt et al., 2014; Rawson et al., 2017,
99 Zhang et al., 2017).

100 In this study we consider the in-situ experiments performed by Zhang et al. (2017) in an
101 As-contaminated aquifer in a sedimentary basin in which the arsenic release from
102 synthesized As-loaded goethite-coated sand was investigated. The results of these
103 experiments suggested that the monitored As release was primarily driven by sorption
104 processes over the 80 days experimental period. Such recently published dataset offers a
105 unique opportunity to test the ability of the DDL and CD-MUSIC models to simulate
106 arsenic sorption under natural hydrochemical and flow-through conditions with sets of
107 surface reactions and affinity constants implemented based on the outcomes of
108 independent batch experiment studies. These SCMs were chosen based on their extensive
109 list of surface reactions for goethite as well as their broad application. To simulate As
110 desorption from the 7 observation wells at the field site we propose a flow-through
111 approach implementing the description of adsorption mechanisms in a complex
112 multicomponent system based on the DDL and CD-MUSIC models. We assess the
113 performance of the two models to reproduce the observed transient decrease and the
114 steady-state of As surface concentrations together with their respective predictions of the
115 change in surface composition. Sensitivity analyses were performed to compare the

description of sorption mechanisms in the respective models as well as to strengthen our understanding of the complex interplay between sorption competition and electrostatic interactions affecting the fate and transport of As in natural groundwater systems.

2. Materials and methods

2.1. In-situ experiments and data set description

In-situ field experiments are important to help bridging the gap between controlled laboratory experiments and field observations. For instance, the in-situ exposure of known mineral phases allows establishing natural anoxic hydrochemical and flow-through conditions that are representative of groundwater systems but experimentally difficult to maintain in the laboratory. Detailed description of the in-situ experiments considered in this study is given in Zhang et al. (2017). Here, we only outline the key methods and results concerning the goethite dataset that is the focus of this investigation. The in-situ experiments were conducted in 7 wells in an aquifer in the Hetao Basin, Inner Mongolia, China. Geochemical investigations performed at this site revealed increasing aqueous As concentration together with a change in the redox conditions from oxic to reducing conditions in the direction of the groundwater flow from the Yin mountains to the Yellow River's flat plain (Guo et al., 2010; Guo et al., 2016; Jia et al., 2014). The wells used in the in-situ experiments are screened in the shallow sandy aquifer at depths ranging from 8 to 30.6 m (Table EA1) in the area of slightly alkaline (i.e., pH [7.6 - 8.1]) and reducing conditions as well as high dissolved As concentrations (i.e., [1.98 - 606] ug/L) with As(III) found as the predominant species (~83%). Chemical composition of

the groundwater was measured three times in all wells during the in-situ experiments (i.e., at 0, 30 and 80 days) and the average groundwater composition is provided in Table EA2.

The goethite-coated sand was synthesized in the laboratory according to the method of Schwertmann and Cornell (2000) and subsequently loaded with arsenate by immersing the solid phase in a 500 mg/L As(V) solution with a solid-to-solution ratio of 50 g coated sand/L. The synthesized As-loaded goethite coated sand had a Fe content of 2.64 mg/g dry coated sand, a bulk density of 2.6 g/cm³ and a porosity of 0.5 (i.e., 21 g goethite/L) as well as an As content of 31 µg/g dry coated sand. The coating of quartz sand with goethite was confirmed by X-ray powder diffraction (XRD) together with scanning electron microscopy (SEM). The As-loaded coated sand was divided into amounts of 0.5 g which were wrapped in a permeable 100-mesh Teflon foil before being deployed and hosted in 7 wells at screen depths (Table EA1) for approximately 80 days. A number of such permeable foils containing the As-loaded goethite-coated sand were placed in each well. In order to assess the transient change in iron mineral composition and As surface concentration due to the flow of the natural groundwater through the goethite-coated porous medium, the individual samples in the wells were collected at successive time steps throughout the duration of the experiment. The total Fe and As contents of the As-bearing goethite-coated sand were measured from two replicates by ICP-AES after total digestion of 0.1 g dry sample using the microwave-assisted method of Link et al. (1998). As K-edge X-Ray absorption (XANES) was applied to determine the As surface oxidation state. The possibility that any potential iron mineral transformation took place

during the in-situ experiments was investigated combining XRD, XANES and SEM analyses (Zhang et al., 2017).

During the experiment, a progressive decrease of the As content in the goethite-coated sand was observed in all monitoring wells as the reactive minerals deployed were flushed by the natural groundwater flow. The analyses performed on the removed samples showed that the total iron content remained the same throughout the experiment and no Fe-oxides other than goethite were detected. Thus, no dissolution and/or transformation of goethite occurred and competitive sorption/desorption mechanisms are the only cause of arsenic release from goethite and As(V) was the only As species present on the goethite at the end of the experiment ($t = 80$ days).

2.2. Geochemical modeling

2.2.1. Modeling approach

Modeling of As release from goethite through sorption competition is performed by simulating the flow of groundwater through the deployed goethite-coated porous medium. Such flow-through conditions lead to the continuous replenishment of dissolved chemical constituents that contact the reactive mineral and cause a transient change in the geochemical conditions and, thus, in the surface composition. Despite the reducing conditions prevailing at the site, the reductive transformation of goethite was shown insignificant by the iron mineral analyses confirming that goethite remained stable during the in-situ experiments. Fig. 1 illustrates the conceptual framework used to simulate the experimentally observed As release from goethite at the site.

The modeling approach can be summarized in the following steps:

- 182 • Simulation of As loading onto goethite by equilibrating the goethite surface with
183 the solution used in the laboratory to prepare the reactive samples of goethite-
184 coated sand deployed in the field.
- 185 • Definition of the groundwater solution according to the average hydrochemical
186 measurements at the field site (Table EA2).
- 187 • Simulation of the advective movement of groundwater through the goethite-
188 coated porous medium samples.
- 189 • Description of sorption/desorption in the flow-through setup assuming local
190 equilibrium and considering surface complexation reactions.
- 191 • Comparison between the simulated and measured As release from the goethite-
192 coated sand in the different wells.
- 193 • Exploration of possible improvement in the agreement with the field data when
194 optimizing surface complexation parameters.
- 195 • Sensitivity analysis of surface composition and sorption mechanisms to
196 groundwater chemical composition.

197

Fig. 1. Illustration of the modeling approach: (a) Sketch of the wells with the goethite samples and parallel calibration of surface complexation parameters, (b) description of solution and surface/solution processes under flow-through conditions, (c) flow chart summarizing the model implementation strategy.

The modeling of the As pre-loading and subsequent desorption from goethite induced by the flow-through conditions and the continuous supply of groundwater aqueous species was implemented with the geochemical code PHREEQC-3 (Parkhurst and Appelo, 2013) coupled with the software MATLAB[®] using the IPhreeqc module (Charlton and Parkhurst, 2011; Muniruzzaman and Rolle, 2016). Coupling these codes allowed us to obtain a flexible simulation tool combining the transport and geochemical calculations capabilities of PHREEQC with the computational methods of MATLAB[®] for parallelizing the simulations, optimizing the set of model parameters, and for performing sensitivity analyses (Haberer et al., 2015; Rolle et al., 2018). The thermodynamic aqueous reactions database WATEQ4F was amended to include some key reactions that might significantly influence the As mobility. In particular, we ensured thermodynamic

consistency between the aqueous and surface complexation reactions defined for arsenic by applying the set of As speciation reactions and constants used by Dixit and Hering (2003) and Stachowicz et al. (2006, 2008). One protonation reaction for phosphate (Smith and Martell, 1976) was added since this aqueous species can strongly influence the As sorption (Dixit and Hering, 2003; see Table EA5 in the Electronic Annex). The flow rates defined through the advective time steps were calibrated within a range of values encompassing the groundwater flow conditions encountered at the field site ([0.01 - 1] m/day; Guo et al., 2016).

2.2.2. Surface complexation

The SCMs proposed in the literature mainly differ in their interfacial structures used to mathematically describe the surface electrostatic field and its influence on the ions present at the solid/solution interface; such ionic species interact electrostatically with the surface of the mineral (Davis et al., 1978; Hayes and Leckie, 1987; Hayes et al., 1990; Davis and Kent, 1990; Goldberg, 1992). In this study, we simulate the in-situ experiments with the approach outlined in the previous section, implementing surface complexation reactions according to the DDL and CD-MUSIC models.

The DDL model is composed of two layers, the surface and the diffuse double layer, to account for (i) complexation reactions (i.e., formation of inner sphere complexes chemically bound to the surface) and (ii) electrostatic interactions between the surface and ions in the bulk solution. However, the DDL model doesn't explicitly account for the position of charged species that electrostatically interact with the surface (i.e., treated as point charges; Davis and Kent, 1990; Goldberg, 1992) whereas it has been shown that

partially dehydrated ions might form ion-specific weak interactions with the surface (Hayes and Leckie, 1987; Hiemstra and van Riemsdijk, 1996). To address this limitation and improve the description of sorption mechanisms, the triple layer model was originally proposed by Yates et al. (1974) and implemented by Davis et al. (1978) with the addition of a Stern layer including two capacitances in-between the surface and the diffuse layer to account for the outer-sphere complexes defined through mass law equations (Hayes and Leckie, 1987; Davis and Kent, 1990; Rahnemaie et al., 2006). Following this extended Stern model representation, the CD-MUSIC model developed by Hiemstra and van Riemsdijk (1996) includes two additional components to describe macroscopic adsorption mechanisms by considering spectroscopic and microscopic information on the structures of the surface and the complexes. The multisite complexation (i.e., MUSIC) component takes into account the coordination, the speciation, and the abundance of the different types of surface functional groups having different affinity for charged species. Furthermore, the concept of charge distribution (i.e., CD) is used to describe the charge distribution of the surface complexes in the interfacial region due to the electrostatic potential gradient that develops normal to the surface. The individual charges of the adsorbed ions are distributed between different planes that delineate distinct layers at the surface/solution interface. Different types of binding (e.g., monodentate, bidentate) are explicitly considered in the CD-MUSIC model as the charge distribution of inner-sphere complexes is derived from the geometry of the complexes through the Pauling bond valence concept (Hiemstra and van Riemsdijk, 1996). The DDL model, instead, only includes monodentate complexes.

In the SCMs, the mineral surfaces are defined by the density of sites of the considered surface groups, the specific surface area and the mass of the considered mineral. The site densities were fixed to proposed literature values while the surface area was calibrated on the experimentally observed transient As desorption. In the DDL model, a single type of surface site for goethite is typically considered (Mathur and Dzombak, 2006). This parameter was set to 2 sites/nm² for consistency with the As complexation reactions and relative affinity constants that were determined by Dixit and Hering(2003). This value is within the range of site densities reported in the literature (1.4 sites/nm² Ali and Dzombak, 1996; 2.3 sites/nm² van Geen et al., 1994). In the CD-MUSIC model, the singly coordinated FeOH(H) and the triply coordinated Fe₃O(H) surface groups of goethite are considered with site densities fixed to 3.45 and 2.7 sites/nm², respectively, for consistency with the CD-MUSIC surface reactions database (Hiemstra and van Riemsdijk, 1996; Hiemstra and van Riemsdijk, 2006; Stachowicz et al., 2008). For both SCMs, the surface area was calibrated within the range [40 - 110] m²/g based on previous literature studies (Hiemstra and van Riemsdijk, 1996; Mathur and Dzombak, 2006).

Extensive surface reaction databases were implemented for the respective SCMs by performing a literature review in order to model the complex geochemical behavior at the surface/solution interface. The set of surface reactions for the DDL model consisted of a series of protonation/deprotonation and complexation reactions with corresponding affinity constants (Table EA3 in the Electronic Annex). The CD-MUSIC database similarly contains surface reactions controlled by law of mass action equations but it additionally allows the description of the charge distribution of a complex at the surface/solution interface. This is done through the definition of charge allocation

parameters among the 3 planes defined in the model (Table EA4 in the Electronic Annex). The contributions of Stachowicz et al. (2006, 2007 and 2008) and Dixit and Hering (2003, 2006) were considered as the base literature for the development of a consistent database for goethite in the CD-MUSIC and DDL models, respectively. These contributions were selected since they represent landmark studies assessing the As sorption onto goethite in single and multi-sorbates aqueous systems. Additional surface reactions and associated parameters were taken from previously published contributions with consideration for thermodynamic consistency. The reader should refer to Tables EA3 and EA4 in the Electronic Annex for a complete overview of the considered references, surface complexation reactions and relative parameters used in the DDL and CD-MUSIC models, respectively. We assessed the ability of the implemented SCM parameters databases to simulate the As desorption by (i) applying the best estimates proposed in individual publications and (ii) exploring the 95% confidence intervals to improve the agreement with the data.

2.2.3. Calibration strategy and sensitivity analyses

To explore possible improvement in reproducing the temporal release of arsenic from goethite when optimizing the SCM parameters, the calibration of the CD-MUSIC and the DDL was performed in two successive levels with different number of calibrated parameters. The first calibration level (i.e., DDL 1 and CD-MUSIC 1) included only the optimization of the flow rates and the goethite surface area. The second calibration level (i.e., DDL 2 and CD-MUSIC 2) additionally comprised the surface complexation parameters (i.e., affinity constants, capacitances, charge allocation coefficients) that were allowed to vary within their confidence interval when reported in literature. The

calibration of the sorption parameters was performed simultaneously by parallelizing the simulations of the 7 different wells used in the field experiments (Fig. 1). All the goethite used in the in-situ experiments and deployed in the different wells was synthesized in the laboratory at the same time (Zhang et al., 2017) and, thus, was considered having identical sorption properties in the simultaneous simulations (Fig. 1). The model parameters were calibrated in the MATLAB[®] environment with an automated procedure minimizing the root mean squared error (RMSE) between simulated and observed As surface concentrations. Due to the high number of parameters and the non-linearity of the problem, the heuristic, global-search particle swarm optimization (PSO) method was chosen to minimize the objective function (Rathi et al., 2017; Rawson et al., 2016).

The mechanisms of sorption competition simulated using the selected SCMs are functions of the aqueous solution composition of the natural groundwater, as well as, of the surface complexation parameters. In order to make model-based interpretations of the key hydrochemical factors controlling As sorption on goethite from calibrated models, we address possible overfitting by fixing to their literature value the parameters that did not lead to significant improvement in the agreement with the measured As surface concentrations. The sensitivity of the goethite surface composition to changes in hydrochemical conditions was tested using the optimized set of model parameters. In this assessment, we performed batch and flow-through simulations of the goethite mineral phase in contact with the groundwater for various aqueous compositions. The method of Morris together with the radial point approach (Sohier et al., 2014) was applied in the sensitivity analyses to test the direct and non-linear impact of the parameters on the model output at low computational cost (Saltelli et al., 2004). Details about this method

and on the design of the sensitivity analyses performed in this study are provided in Section EA-4 in the Electronic Annex.

3. Results

3.1. Arsenic desorption

The field observations of As release from the synthesized goethite-coated sand were simulated with the proposed modeling approach based on both the DDL and CD-MUSIC descriptions of surface complexation reactions. Figure 2 illustrates the comparison between the field measurements in the 7 different wells and the model simulations obtained with the two calibration levels: without (i.e., level 1) and with (i.e., level 2) optimization of the surface complexation constants (i.e., affinity constants, charge allocation and capacitances).

Fig. 2. Measured and simulated temporal change in adsorbed As concentrations in all wells. Calibration level 1: SCM parameters fixed to the best estimate values reported in

the literature; calibration level 2: SCM parameters calibrated within the respective range of values reported in the literature.

The field datasets from the different wells show a transient release of As from goethite; however, the extent of desorption evaluated at different times during the in-situ experiment was found to be different and the decreasing trends of As concentrations on the goethite-coated sand spatially differ as a combined result of the flow and aqueous composition variability among the wells. A satisfying agreement between simulations and observations is obtained using a single set of surface complexation parameters for all observation wells using both the CD-MUSIC and the DDL formulations. Measurement of the goodness-of-fit is provided in section EA-3 of the Electronic Annex. The best fit to the measured As surface concentrations is achieved when using the CD-MUSIC to describe the surface complexation reactions (Fig. 2). This model already provides a satisfactory agreement with the experimental data at the calibration level 1 (i.e., directly using literature values, without the need to calibrate the surface complexation parameters). Successive calibration of these parameters (calibration level 2) only yielded minor improvements (i.e., 3.7% reduction of RMSE). In particular, the CD-MUSIC reproduces best the temporal decrease in the extent of As desorption towards the steady-state As surface concentrations observed in most of the wells (Fig. 2, Section EA-3). The results of the DDL-based approach are different. The model with literature values for the surface complexation parameters (calibration level 1) cannot capture the observed trends in most of the observation wells (i.e., mean absolute relative error of 0.3, Hauduc et al., 2015; continuous orange line in Fig. 2). A successive calibration step, optimizing the surface complexation parameters, is necessary to obtain a significant improvement (i.e.,

34% reduction of RMSE) and a close representation of the observed As surface concentration in all observation wells. This improvement resulted from the calibration of three affinity constants, thus, the remaining constants were fixed to the best estimates reported in the literature (Section EA-4). The optimized set of affinity constants for DDL 2 is provided in Table EA3. Despite the apparent improvement, the calibrated DDL 2 model still cannot capture the leveling of As surface concentrations, approaching steady-state conditions with the flowing groundwater, which was observed in most of the wells at the end of the in-situ experiments (Fig. 2).

The calibrated values of flow rates (See Table EA7 in the Electronic Annex) and surface areas (49.6, 45.8 and 43.6 m²/g, respectively) were found consistent between the models: CD-MUSIC 1, CD-MUSIC 2 and DDL 2, which provided the best representation of the experimental observations, thus, allowing a direct comparison between the DDL and the CD-MUSIC outcomes.

3.2. Surface composition

Once the model parameters were calibrated, the models were run in order to simulate the temporal change in surface composition and to shed light on the surface competition mechanisms affecting As desorption in the different wells. The temporal change in surface composition was analyzed using the fractional site occupancy that expresses the relative amount of sites occupied by a species.

Figure 3 displays the fractional site occupancy for all wells according to the calibrated models at the initial time and at the end of the in-situ experiments (80 days). The models selected are DDL 2 and CD-MUSIC 1, since further calibration of the latter did not result

in significant improvements. The outcomes of the simulations show that the surface compositions are similar among the locations of the observation wells at the field site for a given SCM. Some similarities between the CD-MUSIC and the DDL models outcomes can also be observed. For instance the strong affinity of phosphate ([40 - 50]% and [23 - 38]%, respectively) and iron (30% and [15 - 40]% respectively) for goethite surface sites. However, significant differences generally exist between the simulated surface compositions when using the DDL and the CD-MUSIC approaches. In particular, the DDL model shows significant sorption of Mg^{2+} (i.e., [15 - 33]%) whereas the CD-MUSIC shows a higher fraction of protonated sites (i.e., [6 - 9]%). The DDL model also shows minor adsorptions of Ca^{2+} and HCO_3^- in wells H01-2 and 3-4, respectively, which were not found significant in the simulations performed with the CD-MUSIC.

Fig. 3. Map of the field site with location of the observation wells and fractional site occupancy at $t=80$ days obtained with the CD-MUSIC (red) and DDL (blue). R is the sum of all the remaining elements occupying less than 3% of the total sites. (+) and C denote the protonated sites and sites occupied by carbonate species. Zones 1, 2 and 3 are the areas of oxic, sub-oxic and reducing conditions identified at the field site (Jia et al., 2014).

Since the model results regarding species involved in sorption competition are similar among the different wells for a given SCM, we focus on well 4-5 to assess further the differences between SCM outcomes and the factors responsible for As desorption. The simulation results for the remaining wells can be found in Section EA-3 in the Electronic Annex. Figure 4 displays the dynamic change in surface composition in well 4-5 during the field desorption experiments using the CD-MUSIC and the DDL models.

Fig. 4. Temporal change in surface composition of goethite in well 4-5. (a) and (d): Change in As concentration and As speciation. (b) and (c): Change in fractional site

413 occupancy of the singly and triply coordinated sites, respectively, for the CD-MUSIC.
414 (e): Change in fractional site occupancy of the surface sites for the DDL model. For the
415 CD-MUSIC model, protonated sites (+) were counted as $\equiv\text{FeOH}_2^{+0.5}$ and $\equiv\text{Fe}_3\text{OH}^{+0.5}$, and
416 deprotonated sites (-) were counted as $\equiv\text{FeOH}^{-0.5}$ and $\equiv\text{Fe}_3\text{O}^{-0.5}$. For the DDL model,
417 protonated and deprotonated sites were counted as Goe_OH_2^+ , Goe_OH^- , respectively.

418 In the CD-MUSIC model results, As surface speciation consists both in As(III) and
419 As(V) with a decrease in As(V) surface concentration and an uptake of As(III) (Fig. 4a).
420 In contrast, the DDL model shows almost exclusively As(V) present on the surface (Fig.
421 4d). The adsorbed As(III) in the CD-MUSIC model mostly consists in the ternary
422 complex goethite-Fe(II)-As(III) accounting for more than 80% of the total adsorbed
423 As(III). The As adsorbed on the goethite surface is shown by the CD-MUSIC model to
424 exclusively remain as goethite-Fe(II)-As(III) complex at the end of the in-situ
425 experiments. However, spectroscopy analysis of the sampled material only revealed the
426 presence of As(V) at the surface of goethite (Zhang et al., 2017). To explain this
427 discrepancy, we hypothesize that surface oxidation of As(III) to As(V) occurred through
428 an electron transfer mechanism towards the bulk of the goethite. Such process has already
429 been observed under well-controlled laboratory conditions by Amstaetter et al. (2010)
430 and is likely to play an important role also under the hydrochemical conditions of the in-
431 situ experiment.

432 Regarding As(V) adsorbed onto goethite, both SCMs show an instantaneous change in
433 the surface speciation at initial time when goethite is incubated in the wells. In the CD-
434 MUSIC model, As(V) is equally shared between the bidentate $(\equiv\text{FeO})_2\text{AsO}_2^{-2}$ and the

435 monodentate $\text{FeOAsO}_2\text{OH}^{-1.5}$ complexes when loaded onto goethite in the laboratory
436 whereas it consists mostly of $(\equiv\text{FeO})_2\text{AsO}_2^{-2}$ (80 to 90%) when put into contact with the
437 groundwater at the field site. In the DDL model, the surface speciation of As(V) changes
438 from Goe_HAsO_4^- to Goe_AsO_4^{2-} . The simulated speciation of surface complexes for
439 single species (i.e., As(V), phosphate, iron) is shown in Section EA-3 in the Electronic
440 Annex.

441 Both models show that the desorption of As is paralleled by the adsorption of phosphate
442 suggesting direct competition for the goethite sorption sites between these species. In
443 particular, the CD-MUSIC results show that steady-state is reached for these species at
444 about 80 days in well 4-5. The calculated surface speciation of phosphate with the CD-
445 MUSIC model shows that $(\equiv\text{FeO})_2\text{PO}_2^{2-}$ and $\equiv\text{FeOPO}_2\text{OH}^{-1.5}$ are present in quasi equal
446 proportions (i.e., [50-60]% and [40-50]%, respectively). The results of the DDL model
447 only show the phosphate surface species GoePO_4^{2-} . Furthermore, the comparison between
448 the two models shows that the simulated site occupancy and surface concentration of
449 phosphate is significantly higher in the CD-MUSIC model (e.g., twice as much as in well
450 4-5).

451 Both models also show a significant and rapid change in surface composition when
452 bringing goethite in contact with the groundwater. The SCMs similarly result in a fast
453 uptake of Fe and a quasi-instantaneous decrease of protonated sites. Using the CD-
454 MUSIC approach, Fe sorbs onto goethite as two distinct surface species. The dominant
455 mechanism of iron uptake is the direct bond of Fe with the surface and formation of the
456 bidentate complex $(\equiv\text{FeOH})_2\text{Fe}^+$. This surface species is dominant [50 – 90]%, however

also the ternary monodentate complex involving arsenic and iron $\equiv\text{FeAs}(\text{OH})_3\text{Fe}^{+0.5}$ is present in significant proportion. Finally, both the CD-MUSIC and the DDL models consistently result in sudden changes for deprotonation and magnesium uptake.

3.3. Sensitivity analysis

We present the results assessing the influence of changing hydrochemistry, from the base case of natural groundwater composition measured at the site, on As affinity for goethite surface. We analyze the impact of pH and trace compounds as well as major ions in two distinct sections.

3.3.1. Effects of pH and trace compounds

We investigated the effects of pH, As, PO_4^{3-} and Fe on the simulated surface composition for both SCMs as these aqueous species were shown to have the strongest affinity for the goethite surface according to the modeling of the field As desorption experiments. A series of batch calculations was performed, that consisted in modeling the change in surface composition when varying, one at a time, pH and the concentrations of selected trace compounds. Figure 5 displays the simulation results, using the groundwater chemistry of well 4-5, and illustrates the individual influence of these aqueous species as well as the non-linear behavior of the adsorption mechanisms computed by the DDL and CD-MUSIC models.

Fig. 5. Adsorption isotherms and effect of pH, PO_4^{3-} and Fe on the surface composition using the groundwater chemistry of well 4-5. The first and second rows show the results for the CD-MUSIC and DDL models, respectively.

The As isotherms shown in Fig. 5a and Fig. 5e are similar for both SCMs. However, the DDL model generally shows higher As uptake for lower aqueous As concentrations (i.e., $\text{As} < 4\text{--}8\ \mu\text{M}$) and faster surface site saturation for increasing aqueous As concentration. Furthermore, adsorption of As(III) is only predicted by the CD-MUSIC model and exclusively occurs as goethite-Fe(II)-As(III) under any tested conditions. This complex is favored under higher As(III) aqueous concentrations as well as mildly basic conditions with a maximum at pH 9 similar to the As(III) complexation in absence of Fe(II) (Stachowicz et al., 2008). In both SCMs, the adsorption of As(V) occurs over the entire pH range and increases with more acidic conditions (Fig. 5b and Fig. 5f) in agreement with the findings of Dixit and Hering (2003) and Stachowicz et al. (2006). Under the typical pH range of natural water [6 - 9], the CD-MUSIC calculations indicate that As(V)

491 complex occurs as the non-protonated bidentate complex $(\equiv\text{FeO})_2\text{AsO}_2^{-2}$ [50 – 80]% and
492 to a lower extent as $\equiv\text{FeOAsO}_2\text{OH}^{-1.5}$ [20 - 50]%. Similarly, the DDL suggests a
493 dominance of $\equiv\text{GoeAsO}_4^{-2}$ which is the surface species equivalent to the CD-MUSIC
494 model complex $(\equiv\text{FeO})_2\text{AsO}_2^{-2}$.

495 Besides the strong effect of pH on As adsorption, both SCMs show that a change in pH
496 exerts a primary control on the overall surface composition with a non-linear effect on
497 sorption competition and change in speciation of the surface species (Fig. 5b and 5f).
498 However, significant discrepancies in the change of surface composition can be pointed
499 out between the SCMs in particular regarding the behavior of As and PO_4^{3-} . For instance,
500 at low pH, the computed As surface concentrations are significantly different (i.e., CD-
501 MUSIC model: 20 mmol/kg, DDL model: 75 mmol/kg in well 4-5 at pH 4). Furthermore,
502 PO_4^{3-} and As(V) adsorption have similar behavior but the surface concentration of PO_4^{3-} is
503 significantly higher than As over the range of tested pH in the CD-MUSIC model. A
504 notable difference between the CD-MUSIC and the DDL models is that PO_4^{3-} adsorption
505 is shown to only occur at circumneutral pH by the DDL while the CD-MUSIC shows
506 high sorption of phosphate also under acidic conditions.

507 For both SCMs, PO_4^{3-} is shown to be the major competitor for As sorption sites. The
508 release of As(V) is inversely proportional to the uptake of PO_4^{3-} ; however, phosphate does
509 not have a significant effect on the sorption of As(III), which exclusively occurs as the
510 ternary complex goethite-Fe(II)-As(III) (Fig. 5c and Fig. 5g). For well 4-5, an increase in

PO_4^{3-} from 0 to 10 μM causes a decrease of the As(V) surface concentration by 50 mmol/kg and 25 mmol/kg in the CD-MUSIC and the DDL model, respectively.

In both SCMs, the change in Fe(II) concentration does not affect significantly As(V) sorption. However, increasing Fe(II) concentration enhance the complexation of As(III) as the goethite-Fe(II)-As(III) complex. In particular for well 4-5, increasing Fe(II) from 0 to 100 μM brings the As(III) surface concentration to 70 mmol/kg. In the DDL model, iron is shown to mainly compete with Mg^{2+} whereas in the CD-MUSIC model, the increase of Fe primarily leads to the decrease in protonated sites.

3.3.2. Effects of major ions

Major ions have been shown to significantly influence sorption competition processes through direct competition for sorption sites (Hayes and Leckie, 1987; Stachowicz et al., 2007; Geelhoed et al., 1997) and/or by modifying the mineral surface charge leading to an enhancement in the adsorption of opposite charged species via electrostatic interactions (Stachowicz et al., 2008). The second mechanism is addressed in the CD-MUSIC description of surface complexation by the explicit consideration of the outer-sphere complexes together with the definition of the triply coordinated group and electrostatic 1-plane controlling the charge interactions between cations and anions. Therefore, we tested the effect of Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} on As desorption from goethite and their impact on the surface composition using the CD-MUSIC model. A brief comparison with the DDL model results is given in Section EA-4 in the Electronic Annex.

Figure 6 shows the simulated As desorption for the in-situ experiments when varying individually the major ion concentrations over a range of values relevant for natural groundwater (i.e., [0.1 - 10] mM for Ca^{2+} , Mg^{2+} and SO_4^{2-} and [0.1 - 20 mM] for HCO_3^-). Additionally, a series of batch calculations with varying concentrations of major ions was performed in order to interpret the results of the flow-through system.

Fig. 6. Effect of the major ions on the As sorption behavior simulated using the CD-MUSIC model under the hydrochemical conditions of well 4-5. (a) to (d): Flow-through simulations, the full lines refer to the simulation performed considering groundwater chemistry of well 4-5; dashed-dotted and dotted lines refer to the simulation results obtained with the lowest and the highest values of the tested concentrations, respectively. (e) to (h): Batch calculations spanning the range of variation of the major cations and anions.

Calcium is shown to have the highest effect on the surface composition and, in particular, on As desorption among the considered major ions (Fig. 6a). An increase in Ca^{2+} concentration results in a higher uptake of As(V) and phosphate and reduces the formation of Fe(II) and As(III)-Fe(II) complexes. The effect of a change in Ca^{2+} on the total As concentration is shown to be particularly strong in the batch system (Fig. 6e) at lower calcium concentrations ($< 2 \text{ mM}$), with a significant decrease in As(III)-Fe(II) uptake. Regarding the simulation of in-situ experiments performed with the lowest Ca^{2+} concentration (i.e., 0.1 mM), the combined enhanced decrease in As(V) and the stimulated uptake of As(III) result in a complex pattern of total As desorption. The simulated curve (black dotted line in Fig. 6a) shows an S-shape with an initial steep slope followed by a plateau regime at about 20 days.

Conversely, a change in the aqueous concentration of Mg^{2+} has little effect on arsenic desorption as shown by the minimal variation of the simulated curves for the in-situ flow-through systems (Fig. 6b). The detailed batch simulations (Fig. 6f) show no effect on the goethite-Fe(II)-As(III) complex and surface protonation, and only a slight decrease in the Fe(II) surface concentration likely due to sorption competition. To a lower extent than Ca^{2+} , higher Mg^{2+} concentrations enhance the uptake of As(V) (i.e., $+8 \text{ mmol/kg}$ as $(\equiv\text{FeO})_2\text{AsO}_2^{-2}$) surface concentrations whereas it decreases significantly the phosphate adsorption (i.e., -20 mmol/kg) as shown in the batch calculations (Fig. 6f).

Bicarbonate has an effect on arsenic sorption mainly through its impact on the solution pH (Fig. 5). In these simulations, in which pH was fixed at the measured value of 8.1 in well 4-5, the influence of changing HCO_3^- concentrations is limited (Fig. 6c and Fig. 6g).

The model results suggest that bicarbonate has little to no effect on the As(V) adsorption whereas an increase in the bicarbonate concentrations is shown to lower the adsorption of the ternary complex goethite-Fe(II)-As(III) and $(\equiv\text{FeOH})_2\text{Fe}^+$.

The CD-MUSIC model results show that sulfate has low to negligible influence on arsenic desorption and on the surface composition. These outcomes are in agreement with the findings of Geelhoed et al. (1997).

4. Discussion

The interpretation of the in-situ experiments highlighted discrepancies between the CD-MUSIC and the DDL models. These outcomes and additional tests on established laboratory datasets (Electronic Annex) showed an improved capability of the CD-MUSIC in modeling As sorption onto goethite in complex multicomponent systems. The limitations of the DDL model can be ascribed to the lower structural model complexity relative to the description of the surface electrostatic behavior, as well as to the quality of the sorption reaction database.

Besides assessing the SCMs ability to reproduce the arsenic desorption trends at the field site, simulations were also performed to assess the impact of varying hydrochemical conditions. The outcomes of the simulations show that the change in As surface concentration mainly results from (i) the surface competition between PO_4^{3-} and As(V) and (ii) the As(III) sorption through the complex goethite-Fe(II)-As(III). The sensitivity analysis also highlights the prominent effect of the groundwater chemistry on the surface composition. Many aqueous species play an important role on the extent and rate of As desorption. Their effects are typically complex and nonlinear and might not be directly

visible from the data and forward simulations of field experiments. In particular, the outcomes of the CD-MUSIC model suggest important implications of the major ions on As mobility through the formation of outer-sphere complexes. Such complexes influence the surface charge behavior and ultimately the sorption of trace elements. The performed simulations helped us to disentangle such complex multicomponent effects and to illuminate the important role of pH, PO_4^{3-} and Ca^{2+} and, to a lower extent of Mg^{2+} and HCO_3^- , on As sorption on goethite

For instance, synergic effects between Ca^{2+} , PO_4^{3-} and As were observed based on the modeling of these in-situ experiments, in agreement with previous observations of such interactions in laboratory setups (Stachowicz et al., 2008). Another interesting insight from the performed simulations is the simultaneous increases in As and PO_4^{3-} surface concentrations when increasing Ca^{2+} in the groundwater. Such a behavior may seem counter-intuitive as PO_4^{3-} is expected to be the main competitor for As(V) sorption sites. However, this result can be interpreted through the leading effect of a higher positive charge in the 1-plane introduced by the inner and outer-sphere complexes of Ca^{2+} (Stachowicz et al., 2008) resulting in a higher surface affinity for As(V) and PO_4^{3-} having both negative charges (i.e., $\Delta_{z_1} = -1.47$ for the dominant As(V) surface species; $\Delta_{z_1} = -1.46$ and -1.28 for the main phosphate species under the considered aqueous conditions ($\equiv\text{FeOH})_2\text{PO}_2^{-2}$ and $\text{FeOPO}_2\text{OH}^{-1.5}$). Indeed, higher Ca^{2+} concentrations result in significantly higher surface charge density in the 1-plane that is compensated by a decrease in surface charge density on the 0-plane (Figure EA14a in the Electronic

Annex). Thus, the model suggests that, for the considered hydrochemical conditions, this electrostatic effects can hamper the sorption competition between As(V) and PO_4^{3-} .

Furthermore, our modeling results indicate significant inverse effect of Ca^{2+} on the Fe complexes and in particular on the ternary complex goethite-Fe(II)-As(III). The presence of Ca^{2+} introduces a higher positive charge in the 1-plane and limits, by electrostatic repulsion, the formation of the Fe(II)-As(III) surface complex ($\Delta_{z_1} = 0.92$) and the Fe surface complex ($\Delta_{z_1} = 1.27$). In contrast, Stachowicz et al. (2008) observed an increase in the adsorption of As(III) in the presence of Ca^{2+} in dual-adsorbate experiments due to their opposite charges. Thus, besides the potential oxidation of As(III) occurring through the formation of the ternary complex goethite-Fe(II)-As(III), the latter exhibits an opposite surface charge behaviour than single As(III) complexes.

As indicated by the CD-MUSIC model, the presence of dissolved ferrous iron seems to be particularly important under the in-situ conditions by primarily enhancing the As(III) adsorption whereas the complex hydrochemistry of the groundwater appears to prevent the direct sorption of As(III) onto goethite. In particular, PO_4^{3-} is known to strongly compete for As(III) sorption sites (Stachowicz et al., 2008) while the CD-MUSIC model based on the field data indicates that the effect of PO_4^{3-} on the goethite-Fe(II)-As(III) complex is negligible. Specifically, the highest As surface concentration at 80 days was measured in well 4-5 with the highest PO_4^{3-} concentration.

630 Regarding Mg^{2+} , Stachowicz et al. (2008) observed similar surface interaction with trace
631 compounds in dual-sorbate system, when compared to Ca^{2+} , due to induced charge
632 effects and successfully captured the sorption processes with the CD-MUSIC model.
633 Using the same description of the surface chemical reactions in our model, an increase in
634 Mg^{2+} uptake is shown to conversely lower the PO_4^{3-} adsorption and, consequently, to
635 favor the As(V) adsorption under the field hydrochemical conditions of the present study.
636 This disagreement about the influence of Mg^{2+} on the adsorption mechanisms can be
637 ascribed to the difference in the electrolyte solutions. For the groundwater solution,
638 containing a larger variety and amount of major ions, the influence of Mg^{2+} on the
639 surface charge is shown to be hindered (Figure EA14b in the Electronic Annex).

640 The role of bicarbonate on As desorption from Fe-oxides has been a matter of debate
641 (Appelo et al., 2002; Stachowicz et al., 2007; Radu et al., 2005; Rahnemaie et al., 2007;
642 Stachowicz et al., 2007). Our modeling results suggest that HCO_3^- has negligible effects
643 on the As(V) adsorption under the environmental hydrochemical conditions at this field
644 site. However, HCO_3^- is shown to lower the adsorption of the ternary complex goethite-
645 Fe(II)-As(III) and $(\equiv\text{FeOH})_2\text{Fe}^+$ although this effect primarily results from the increase
646 in surface site protonation similar to the effect of a change in pH on the change in surface
647 composition (Fig. 6c and Fig. 6g).

648 Despite the complex interplay between many aqueous species taking place in sorption
649 processes, the outcomes of surface complexation modeling can be used to interpret the
650 impact of groundwater hydrochemistry on arsenic transport and mobility in As-
651 contaminated reducing groundwaters. Table 1 reports the concentrations of important

652 groundwater species as well as the As surface concentrations on goethite simulated with
653 the CD-MUSIC model for the field groundwater conditions from well 4-5 as well as
654 reported in two previous studies (Jessen et al., 2012; Biswas et al., 2014). In those
655 contributions, CD-MUSIC simulations were performed to help understanding field
656 observations by considering the surface interactions between groundwater species and
657 sedimentary Fe-oxides and showed that the complexation of goethite-Fe(II)-As(III) was
658 the dominant mechanism of As(III) uptake in the Red River flood plain (Jessen et al.,
659 2012) and in the Bengal Basin (Biswas et al., 2014). Regarding the in-situ hydrochemical
660 conditions of the present study, the maximum remaining As surface concentrations (9.55
661 $\mu\text{g/g}$ compared to an average of 3.32 $\mu\text{g/g}$) was detected in well 4-5, in which the highest
662 pH (i.e., 8.1) was measured. In comparison, Jessen et al. (2012) and Biswas et al. (2014)
663 simulated lower As(III) surface concentration for goethite at equilibrium with
664 groundwater having circumneutral pH and higher Ca^{2+} concentrations which represent
665 hydrochemical conditions that are less favorable for the formation of the goethite-Fe(II)-
666 As(III) as shown in Section 3.3. Surface composition calculation of goethite using the
667 groundwater composition of well 4-5 and applying similar goethite concentration (i.e.,
668 0.3 mmol sites/L) to Jessen et al. (2012) and Biswas et al. (2014) did not lead to
669 significant change in the surface coverage of As. Conversely, when changing pH to 7,
670 significantly less As(III) uptake was obtained (i.e., 1.34 %) similarly to the surface sites
671 occupancy found in the studies of Jessen et al. (2012) and Biswas et al. (2014) despite the
672 substantially higher As(III) concentrations in well 4-5. Thus, pH is likely to represent a
673 determining parameter for the mobility of As(III) through the formation of the complex
674 goethite-Fe(II)-As(III). Furthermore, the concentrations of Fe(II) reported in Jessen et al.

(2012) and Biswas et al. (2014) are significantly higher than in well 4-5 suggesting that uptake of As(III) might remain significant at low Fe level as shown in Section 3.3.1.

Table 1: Comparison of the concentrations of relevant aqueous species and resulting As(V) and As(III) fractional site occupancies on goethite at equilibrium simulated with the CD-MUSIC model in different studies.

Location	This study (well 4-5) Hetao Basin	Biswas et al. (2014) Bengal Basin	Jessen et al. (2012) Red River flood plain
[mmol sites /L]	5.73	0.24	0.31
pH	8.1	7.2	6.98
As(III) [$\mu\text{g/L}$]	535	138	187
As(V) [$\mu\text{g/L}$]	5.75	10	44.95
PO_4^{3-} [$\mu\text{g/L}$]	382	260	759.76
Fe(II) [mg/L]	0.19	5	10.42
HCO_3^- [mg/L]	623	480	537
Ca^{2+} [mg/L]	23	90	112.22
Mg^{2+} [mg/L]	30.1	25	31.59
As(V) [%]	7.3	0	6
Fe(II)-As(III) [%]	6.3	1.4	2

4.1. Global sensitivity

Finally, in order to illustrate the relative linear and non-linear effects of the individual aqueous species on arsenic sorption, we have performed a global sensitivity analysis by applying the Morris method to the field As desorption models of the 7 different wells. Using this approach, two model estimates are obtained: (i) μ expresses the overall importance of the model parameters on the model output; (ii) σ expresses the non-linear effects of the tested parameters and their mutual interactions.

689

690 Fig. 7. Relative importance of pH, PO₄³⁻, Fe, Ca²⁺, Mg²⁺, HCO₃⁻ and SO₄²⁻ on the
691 adsorption/desorption of the As species onto goethite.

692 The results of the global sensitivity analysis are shown in Figure 7 and can be
693 summarized in the following points:

- 694 • As(V) sorption is shown to be predominantly controlled by pH and PO₄³⁻ although
695 it can be noted that the CD-MUSIC model slightly differ from the DDL model as
696 it indicates a stronger effect of PO₄³⁻ on As(V) (Fig. 7c and 7d).
- 697 • pH is shown to have the strongest effect on the As(III) uptake in both SCMs. In
698 contrast, PO₄³⁻ has a negligible influence in the CD-MUSIC (Fig 7a) which
699 simulate the sorption of As(III) as goethite-Fe(II)-As(III). Conversely, in the DDL
700 model PO₄³⁻ seems to have a significant effect on the As(III) uptake although, as

shown in Section 3.3, this surface complexation model shows very low adsorption of As(III) for the considered hydrochemical conditions.

- Fe has a significant effect on the As(III) adsorption for both SCMs (Fig 7a and 7b) whereas it doesn't influence the As(V) sorption (Fig. 7c and 7d).
- The major ions are also shown to have negligible influence on the As sorption in the DDL model whereas some of these species are shown to play an important role by the CD-MUSIC model. For instance, Ca^{2+} influences the sorption of As(III) and As(V) (Fig. 7a and 7b) and HCO_3^- is shown to exert a control on the sorption of As(III) (Fig. 7a).
- None of the tested species is shown to have purely linear or non-linear effects on the As desorption, although non-linear effects of HCO_3^- and Ca^{2+} on the sorption of As(III) seems to be more pronounced (Fig. 7a).

5. Conclusions

In this study, we compared the capabilities of two common SCMs (i.e., the DDL and the CD-MUSIC models) to simulate the arsenic desorption from synthesized goethite-coated sand under natural hydrochemical conditions monitored in a reducing As-contaminated aquifer with respect to the complex interactions occurring at the solution-mineral interface. The focus was on a partially controlled system involving a well-known synthetic mineral phase but natural groundwater chemistry and, thus, complex multispecies interactions in the pore water and at the surface/solution interface. The modeling of such system, of intermediate complexity compared to traditional laboratory

experiments and field investigations, can provide important insights on the factors influencing the mobility of As in groundwater.

Arsenic field desorption at the 7 spatial locations of the considered in-situ experiment was successfully simulated with a modeling approach considering flow-through conditions, surface complexation and groundwater hydrochemistry. Parallelization and optimization of the simulations allowed us to obtain a single set of parameters for all observation wells. The proposed approach is a valuable tool that can be exported to other field sites with different groundwater conditions. Using the dataset of the in situ experiments performed in the Hetao basin (China), we demonstrated the capability of the proposed modeling approach to reproduce arsenic concentrations measured at the surface of goethite under natural hydrochemical conditions. However, the comparison between the description of surface complexation reactions with CD-MUSIC and DDL formulations highlights important differences between the two models for the considered conditions. This suggests that the choice of the SCM can have important implications on the interpretation of experimental observations and on the assessment of As mobility in aquifer systems. In particular, the better agreement between the CD-MUSIC simulations and the field observations at all considered spatial locations indicates the enhanced capability of this SCM to describe the complex interactions between charged species at the mineral/solution interface. This capability relates to the higher structural complexity of the CD-MUSIC model that explicitly accounts for the multiple mineral surface coordination groups and has a more comprehensive representation of the electrostatic interaction at the mineral-solution interface. The CD-MUSIC surface reactions database also seems more suitable for simulating the sorption processes at the goethite surface in

natural hydrochemical systems due to its implementation based on experimental observations of multicomponent systems.

Regarding the complex interplay between charged species in sorption processes, the explicit consideration of direct and indirect effects from chemical and electrostatic interactions is required to accurately assess and predict the mobility of contaminants in the subsurface. To this end, SCMs represent a considerable progress in comparison to the traditional empirical sorption modeling approaches; however, their implementation and validation in complex multicomponent flow-through systems are still rare. This study has focused on goethite but we think that the implementation of surface complexation databases for other relevant mineral phases, with a careful assessment of their performance in multicomponent systems, will be of primary importance to improve the descriptions of the mechanisms of contaminant sorption and release. This will enhance our capability to represent and capture the key role of electrostatic interactions between charged groundwater constituents both at the surface-solution interface and within the pore water (Hiemstra and van Riemsdijk, 1996; Stachowicz et al., 2008; Rolle et al., 2013; Muniruzzaman and Rolle, 2015). The quantitative description of such important mechanisms will strengthen our capability to assess contaminant release, transport, and fate, in complex, multidimensional, physically and chemically heterogeneous groundwater systems (Wang et al., 2018; Fakhreddine et al., 2016; Wen and Li, 2018; Ye et al., 2015).

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