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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, PO₄³⁻ and Ca²⁺ on As sorption
ABSTRACT

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

The model outcomes and the exploration of the sensitivity of the goethite surface composition to changes in hydrochemical conditions provide insights into the 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;
Appelo and Postma, 2005). Surface complexation reactions databases are traditionally implemented based on well-controlled laboratory experiments performed with a low number of aqueous species (Hayes et al., 1990; Dixit and Hering, 2003; Dzombak and Morel, 1990; Mathur and Dzombak, 2006). In contrast, model-based interpretation of As sorption behavior in multi-sorbate systems remain challenging as the interactions between aqueous charged species can be strong, resulting in a complex, nonlinear sorption behavior (Stachowicz et al., 2008). For instance, Dixit and Hering (2006) successfully modeled the sorption of As(III) and Fe(II) individually but had difficulties in reproducing the observations in dual-adsorbates systems using the diffuse double layer (DDL) model. Stachowicz et al. (2008) satisfactorily modeled the sorption of As, Ca^{2+}, Mg^{2+}, PO_4^{3-} and HCO_3^- in dual and triple adsorbate batch systems with the CD-MUSIC model and determined a single set of surface complexation parameters from observations of the individual species. These promising results, towards the implementation of SCMs that can provide accurate predictions under variable hydrochemical conditions, stems from the consideration of microscopic information (i.e., surface and complexes structure) and electrostatic interaction between charged species at the mineral surface in the CD-MUSIC model. A few studies performed evaluations of field datasets by using the ferrihydrite DDL and goethite CD-MUSIC models to estimate the competitive sorption processes taking place on sediments of As contaminated aquifers (Jessen et al., 2012, Biswas et al., 2014). However, the applicability of SCMs with surface complexation constants typically determined from observations on single-sorbate systems to simulate sorption on pure mineral phases in groundwater aquifers involving complex hydrochemistry as well as flow conditions has not been rigorously tested. Therefore,
studies with an intermediate level of complexity are of importance to understand the complex coupling between surface and solution chemistry, electrostatic interactions and mass transfer processes in groundwater systems, and to assess the ability and limitations of SCMs. Such studies include controlled flow-through laboratory experiments (e.g., Tufano and Fendorf, 2008; Sharma et al., 2011; Muniruzzaman et al., 2014; Li et al., 2014) as well as pilot scale field experiments (Neidhardt et al., 2014; Rawson et al., 2017, Zhang et al., 2017).

In this study we consider the in-situ experiments performed by Zhang et al. (2017) in an As-contaminated aquifer in a sedimentary basin in which the arsenic release from synthetized As-loaded goethite-coated sand was investigated. The results of these experiments suggested that the monitored As release was primarily driven by sorption processes over the 80 days experimental period. Such recently published dataset offers a unique opportunity to test the ability of the DDL and CD-MUSIC models to simulate arsenic sorption under natural hydrochemical and flow-through conditions with sets of surface reactions and affinity constants implemented based on the outcomes of independent batch experiment studies. These SCMs were chosen based on their extensive list of surface reactions for goethite as well as their broad application. To simulate As desorption from the 7 observation wells at the field site we propose a flow-through approach implementing the description of adsorption mechanisms in a complex multicomponent system based on the DDL and CD-MUSIC models. We assess the performance of the two models to reproduce the observed transient decrease and the steady-state of As surface concentrations together with their respective predictions of the 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 synthetized 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 synthetized 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:
• Simulation of As loading onto goethite by equilibrating the goethite surface with the solution used in the laboratory to prepare the reactive samples of goethite-coated sand deployed in the field.

• Definition of the groundwater solution according to the average hydrochemical measurements at the field site (Table EA2).

• Simulation of the advective movement of groundwater through the goethite-coated porous medium samples.

• Description of sorption/desorption in the flow-through setup assuming local equilibrium and considering surface complexation reactions.

• Comparison between the simulated and measured As release from the goethite-coated sand in the different wells.

• Exploration of possible improvement in the agreement with the field data when optimizing surface complexation parameters.

• Sensitivity analysis of surface composition and sorption mechanisms to groundwater chemical composition.
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/nm$^2$ 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/nm$^2$ Ali and Dzombak, 1996; 2.3 sites/nm$^2$ van Geen et al., 1994). In the CD-MUSIC model, the singly coordinated FeOH(H) and the triply coordinated Fe$_3$O(H) surface groups of goethite are considered with site densities fixed to 3.45 and 2.7 sites/nm$^2$, 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] m$^2$/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 synthetized 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 synthetized 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).

![Figure 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...](image-url)
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 occupancy.
occupancy of the singly and triply coordinated sites, respectively, for the CD-MUSIC.

(e): Change in fractional site occupancy of the surface sites for the DDL model. For the CD-MUSIC model, protonated sites (+) were counted as $\equiv$FeOH$_2^{+0.5}$ and $\equiv$Fe$_3$OH$^{+0.5}$, and deprotonated sites (-) were counted as $\equiv$FeOH$^{-0.5}$ and $\equiv$Fe$_3$O$^{-0.5}$. For the DDL model, protonated and deprotonated sites were counted as Goe$_{-1}$OH$^+_2$, Goe$_{-1}$OH$^-$, respectively.

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

Regarding As(V) adsorbed onto goethite, both SCMs show an instantaneous change in the surface speciation at initial time when goethite is incubated in the wells. In the CD-MUSIC model, As(V) is equally shared between the bidentate ($\equiv$FeO)$_2$AsO$_2^2$ and the
monodentate FeOAsO$_2$OH$^{-1.5}$ complexes when loaded onto goethite in the laboratory whereas it consists mostly of (≡FeO)$_2$AsO$_2^2$ (80 to 90%) when put into contact with the groundwater at the field site. In the DDL model, the surface speciation of As(V) changes from Goe$_3$HAsO$_4$ to Goe$_3$AsO$_4^{2-}$. The simulated speciation of surface complexes for single species (i.e., As(V), phosphate, iron) is shown in Section EA-3 in the Electronic Annex.

Both models show that the desorption of As is paralleled by the adsorption of phosphate suggesting direct competition for the goethite sorption sites between these species. In particular, the CD-MUSIC results show that steady-state is reached for these species at about 80 days in well 4-5. The calculated surface speciation of phosphate with the CD-MUSIC model shows that (≡FeO)$_2$PO$_2^{2-}$ and ≡FeOPO$_2$OH$^{-1.5}$ are present in quasi equal proportions (i.e, [50-60]‰ and [40-50]‰, respectively). The results of the DDL model only show the phosphate surface species GoePO$_4^{2-}$. Furthermore, the comparison between the two models shows that the simulated site occupancy and surface concentration of phosphate is significantly higher in the CD-MUSIC model (e.g., twice as much as in well 4-5).

Both models also show a significant and rapid change in surface composition when bringing goethite in contact with the groundwater. The SCMs similarly result in a fast uptake of Fe and a quasi-instantaneous decrease of protonated sites. Using the CD-MUSIC approach, Fe sorbs onto goethite as two distinct surface species. The dominant mechanism of iron uptake is the direct bond of Fe with the surface and formation of the bidentate complex (≡FeOH)$_2$Fe$^+$. This surface species is dominant [50 – 90]‰, however
also the ternary monodentate complex involving arsenic and iron $≡\text{FeAs(OH)}_3\text{Fe}^{+0.5}$ 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, $\text{PO}_4^{3-}$ 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, \( \text{PO}_4^{3-} \) 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., \( \text{As} < 4-8 \, \mu\text{M} \)) 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)
complex occurs as the non-protonated bidentate complex ($\equiv$FeO)$_2$AsO$_2^2$ [50 – 80]% and
to a lower extent as $\equiv$FeOAsO$_2$OH$^{-1.5}$ [20 - 50]%. Similarly, the DDL suggests a
dominance of $\equiv$GoeAsO$_4^2$ which is the surface species equivalent to the CD-MUSIC
model complex ($\equiv$FeO)$_2$AsO$_2^2$.

Besides the strong effect of pH on As adsorption, both SCMs show that a change in pH
exerts a primary control on the overall surface composition with a non-linear effect on
sorption competition and change in speciation of the surface species (Fig. 5b and 5f).
However, significant discrepancies in the change of surface composition can be pointed
out between the SCMs in particular regarding the behavior of As and PO$_4^{3-}$. For instance,
at low pH, the computed As surface concentrations are significantly different (i.e., CD-
MUSIC model: 20 mmol/kg, DDL model: 75 mmol/kg in well 4-5 at pH 4). Furthermore,
PO$_4^{3-}$ and As(V) adsorption have similar behavior but the surface concentration of PO$_4^{3-}$ is
significantly higher than As over the range of tested pH in the CD-MUSIC model. A
notable difference between the CD-MUSIC and the DDL models is that PO$_4^{3-}$ adsorption
is shown to only occur at circumneutral pH by the DDL while the CD-MUSIC shows
high sorption of phosphate also under acidic conditions.

For both SCMs, PO$_4^{3-}$ is shown to be the major competitor for As sorption sites. The
release of As(V) is inversely proportional to the uptake of PO$_4^{3-}$; however, phosphate does
not have a significant effect on the sorption of As(III), which exclusively occurs as the
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.

![Flow-through simulations](image1)

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 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 mmol/kg as \(\equiv FeO\)\(_2\)AsO\(_4\)) 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 \(\text{PO}_4^{3-}\) 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 ($\equiv$FeOH)$_2$PO$_2^2$ and FeOPO$_2$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.
Regarding Mg\(^{2+}\), Stachowicz et al. (2008) observed similar surface interaction with trace compounds in dual-sorbate system, when compared to Ca\(^{2+}\), due to induced charge effects and successfully captured the sorption processes with the CD-MUSIC model. Using the same description of the surface chemical reactions in our model, an increase in Mg\(^{2+}\) uptake is shown to conversely lower the PO\(_4^{3-}\) adsorption and, consequently, to favor the As(V) adsorption under the field hydrochemical conditions of the present study. This disagreement about the influence of Mg\(^{2+}\) on the adsorption mechanisms can be ascribed to the difference in the electrolyte solutions. For the groundwater solution, containing a larger variety and amount of major ions, the influence of Mg\(^{2+}\) on the surface charge is shown to be hindered (Figure EA14b in the Electronic Annex).

The role of bicarbonate on As desorption from Fe-oxides has been a matter of debate (Appelo et al., 2002; Stachowicz et al., 2007; Radu et al., 2005; Rahnemaie et al., 2007; Stachowicz et al., 2007). Our modeling results suggest that HCO\(_3^-\) has negligible effects on the As(V) adsorption under the environmental hydrochemical conditions at this field site. However, HCO\(_3^-\) is shown to lower the adsorption of the ternary complex goethite-Fe(II)-As(III) and (≡FeOH\(_2\))Fe\(^+\) although this effect primarily results from the increase in surface site protonation similar to the effect of a change in pH on the change in surface composition (Fig. 6c and Fig. 6g).

Despite the complex interplay between many aqueous species taking place in sorption processes, the outcomes of surface complexation modeling can be used to interpret the impact of groundwater hydrochemistry on arsenic transport and mobility in As-contaminated reducing groundwaters. Table 1 reports the concentrations of important
groundwater species as well as the As surface concentrations on goethite simulated with the CD-MUSIC model for the field groundwater conditions from well 4-5 as well as reported in two previous studies (Jessen et al., 2012; Biswas et al., 2014). In those contributions, CD-MUSIC simulations were performed to help understanding field observations by considering the surface interactions between groundwater species and sedimentary Fe-oxides and showed that the complexation of goethite-Fe(II)-As(III) was the dominant mechanism of As(III) uptake in the Red River flood plain (Jessen et al., 2012) and in the Bengal Basin (Biswa et al., 2014). Regarding the in-situ hydrochemical conditions of the present study, the maximum remaining As surface concentrations (9.55 μg/g compared to an average of 3.32 μg/g) was detected in well 4-5, in which the highest pH (i.e., 8.1) was measured. In comparison, Jessen et al. (2012) and Biswas et al. (2014) simulated lower As(III) surface concentration for goethite at equilibrium with groundwater having circumneutral pH and higher Ca^{2+} concentrations which represent hydrochemical conditions that are less favorable for the formation of the goethite-Fe(II)-As(III) as shown in Section 3.3. Surface composition calculation of goethite using the groundwater composition of well 4-5 and applying similar goethite concentration (i.e., 0.3 mmol sites/L) to Jessen et al. (2012) and Biswas et al. (2014) did not lead to significant change in the surface coverage of As. Conversely, when changing pH to 7, significantly less As(III) uptake was obtained (i.e., 1.34 %) similarly to the surface sites occupancy found in the studies of Jessen et al. (2012) and Biswas et al. (2014) despite the substantially higher As(III) concentrations in well 4-5. Thus, pH is likely to represent a determining parameter for the mobility of As(III) through the formation of the complex 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.

<table>
<thead>
<tr>
<th>Location</th>
<th>This study (well 4-5)</th>
<th>Biswas et al. (2014)</th>
<th>Jessen et al. (2012)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[mmol sites /L]</td>
<td>[mmol sites /L]</td>
<td>[mmol sites /L]</td>
<td>[mmol sites /L]</td>
</tr>
<tr>
<td>pH</td>
<td>8.1</td>
<td>7.2</td>
<td>6.98</td>
</tr>
<tr>
<td>As(III) [μg/L]</td>
<td>535</td>
<td>138</td>
<td>187</td>
</tr>
<tr>
<td>As(V) [μg/L]</td>
<td>5.75</td>
<td>10</td>
<td>44.95</td>
</tr>
<tr>
<td>PO₄³⁻ [μg/L]</td>
<td>382</td>
<td>260</td>
<td>759.76</td>
</tr>
<tr>
<td>Fe(II) [mg/L]</td>
<td>0.19</td>
<td>5</td>
<td>10.42</td>
</tr>
<tr>
<td>HCO₃⁻ [mg/L]</td>
<td>623</td>
<td>480</td>
<td>537</td>
</tr>
<tr>
<td>Ca²⁺ [mg/L]</td>
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</tr>
<tr>
<td>As(V) [%]</td>
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<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Fe(II)-As(III) [%]</td>
<td>6.3</td>
<td>1.4</td>
<td>2</td>
</tr>
</tbody>
</table>

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.
Fig. 7. Relative importance of pH, PO$_4^{3-}$, Fe, Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$ and SO$_4^{2-}$ on the adsorption/desorption of the As species onto goethite.

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

- As(V) sorption is shown to be predominantly controlled by pH and PO$_4^{3-}$ although it can be noted that the CD-MUSIC model slightly differ from the DDL model as it indicates a stronger effect of PO$_4^{3-}$ on As(V) (Fig. 7c and 7d).

- pH is shown to have the strongest effect on the As(III) uptake in both SCMs. In contrast, PO$_4^{3-}$ has a negligible influence in the CD-MUSIC (Fig 7a) which simulate the sorption of As(III) as goethite-Fe(II)-As(III). Conversely, in the DDL model PO$_4^{3-}$ 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\textsuperscript{2+} influences the sorption of
As(III) and As(V) (Fig. 7a and 7b) and HCO\textsubscript{3}\textsuperscript{-} 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\textsubscript{3}\textsuperscript{-} and Ca\textsuperscript{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 synthetized 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).
Acknowledgments

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