Metals and Metalloid Removal by Colloidal Humic Acid–Goethite: Column Experiments and Geochemical Modeling

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Reactive barriers are proposed to scavenge groundwater contaminants such as metals and arsenate. Their remediation capacity is commonly investigated with sorption data disregarding the complexity of the interactions among elements when faced with mixed contamination. This study was set up to measure interactions during reactive transport of the anionic arsenate As(V) and cationic metals and test if that transport can be modeled with geochemical codes. Sand coated with colloidal humic acid–goethite was the adsorbent in line with field work where these colloidal particles have been injected in situ. Equilibrium batch adsorption experiments showed binding preferences in the order: As(V) >> Cu > Zn > Cd > Ni. Column experiments with single and binary mixtures showed an important synergistic effect of As(V) on Zn sorption but the reverse interaction was not found; this interaction is not included in the PHREEQC geochemical code. The breakthrough curves (BTCs) of mixtures of As(V), Cd, Cu, Ni, and Zn showed that Cd and Ni concentrations in the effluent exceeded those of the influent, an overshooting effect attributed to competition among divalent cations. Simulations with the PHREEQC geochemical code using a surface complexation model for sorption reactions on goethite and humic acids coupled to the transport module successfully predicted the most essential trends of the BTCs, illustrating the potential of these codes to estimate the longevity of the reactive barriers used to remediate mixtures of contaminants. The novel aspect of this work is that a correct reactive transport model in PHREEQC was obtained by only adjusting the number of reactive surface sites of the adsorbent from fitting batch sorption distribution coefficient ($K_d$) values.

Abbreviations: BTCs, breakthrough curves; HA-Goe, humic acid goethite; HFO, hydrous ferric oxide; ICP–MS, inductively coupled plasma mass spectrometry; MES, 2-(N-morpholino)ethanesulfonic acid; MOPS, 3-(N-morpholino)propanesulfonic acid; PVs, pore volumes; WHAM, Windermere’s humic acid model.

Heavy metals and metalloids are the major contaminants affecting groundwater bodies in Europe (van Liedekerke et al., 2014). Metals such as Cd, Cu, Ni, and Zn as well as metalloids such as As can be present in contaminated sites as a result of anthropogenic activities (e.g., agriculture, mining, smelting industries) and are of concern because of their toxicity (Tchounwou et al., 2012). Protecting groundwater from pollution and restoring contaminated sites is of the highest importance around the globe, considering that about 75% of the public water supply relies on this resource (European Commission, 2008). Managing groundwater pollution has proved to be very challenging, and knowledge about sorption and transport of contaminants is needed to develop effective remediation strategies.

Nanoremediation involves the application of colloidal (1–1000 nm) materials; it has gained great interest as a cost-effective technology for in situ treatment of contaminated groundwater (Karn et al., 2009). Engineered Fe(III) oxide nanoparticles (e.g., goethite, hematite, ferrihydrite) are among the materials proposed and developed for remediation of groundwater from heavy metals and metalloids (Cundy et al., 2008). These particles can be injected in the groundwater and can be immobilized by flocculation and/or retention, thereby forming an in situ reactive barrier. The advantages of Fe oxides are their strong affinity to adsorb both metallic cations (e.g., Cd, Zn) and oxyanions [e.g., As(V)] as well as high adsorption capacity due to their large reactive surface area.
The adsorption of the main contaminants of groundwater (e.g., As, Cd, Cu, Ni, and Zn) on Fe oxides, particularly goethite, is well studied, and its sorption reactions are embedded in geochemical models that are validated with environmental data. Different elements logically compete for sorption on the reactive surface, and such interactions have environmental significance. For example, cation competition among trace metals for sorption on the reactive barriers may yield effluent concentration overshooting effects in the long term. Overshooting is a chromatographic phenomenon that has been described in columns receiving multi-metal mixture solutions and is explained by competitive ion exchange, where the metal with the higher affinity for adsorption causes desorption or displacement of the metal with the lower affinity (Figueira et al., 2000; Kratochvil and Volesky, 2000). That overshooting is evidenced by higher concentrations of the weakly adsorbed metal in the effluent than those in the influent solution because of displacement by the more strongly adsorbed metal (peak at relative concentration $C/C_0 > 1$). In natural contaminated water, mixed contamination is the rule rather than the exception, hence these interactions need to be accounted for. Batch sorption data have revealed synergistic sorption between divalent cations (e.g., Cd$^{2+}$, Zn$^{2+}$) and the anionic arsenate As(V) (Gräfe et al., 2004; Jiang et al., 2013).

The enhanced sorption of cations and oxyanions due to synergism has been explained by surface co-precipitation, i.e., the formation of adamite-like compounds [Zn$_2$(AsO$_4$)OH] on the surface of goethite (Gräfe et al., 2004) when solution concentrations are above site saturation. At solution concentrations below surface site saturation, the enhanced sorption has been attributed to the formation of ternary cation–anion surface complexes, i.e., Cd–As(V)–goethite complexes (Jiang et al., 2013). Along the same lines, competition (antagonism) among different cationic metals for sorption on Fe minerals such as goethite are well established in batch systems (Christophi and Axe, 2000).

The extent of retardation of contaminants in transport experiments has been usually described by empirical linear ($K_d$) and nonlinear (e.g., Freundlich, Langmuir) adsorption models combined with the convection–dispersion equation and either equilibrium or kinetic considerations (Chotparkar et al., 2011; Seuntjens et al., 2001). Such empirical models have been extended to account for competitive sorption reactions, but these models are not capable of simulating reactions outside the specific chemical conditions under which the model parameters were derived (Selim and Zhang, 2013). Alternatively, surface complexation models or ion exchange models can quantify adsorption and describe competitive reactions under a wider range of chemical conditions (Goldberg et al., 2007). The shortcoming is that mechanistic models are not able to describe time-dependent reactions (Selim and Zhang, 2013). The ability to predict the fate of contaminants under variable chemical conditions would allow a better assessment of remediation technologies and their potential use in the field. The interactions among cationic metals during reactive transport has been studied with column experiments and modeled with geochemical codes (Dijkstra et al., 2008; Hanna et al., 2009; Voegelin et al., 2003). Surprisingly, only a limited number of studies have investigated reactive transport of metal cations and the anionic arsenate, and the examples found are mostly limited to soils with no geochemical modeling included (Hu et al., 2010; Kim et al., 2016). Colloidal Fe oxides, either coated or not with additional organic matter, are candidate sorbents for groundwater contamination at sites where toxic metals and metalloids occur as mixtures, hence the metal–metalloid interaction needs to be studied.

This study was set up to measure interactions during reactive transport of the anionic arsenate and cationic metals and test if that transport can be modeled with geochemical codes. Single, binary, and multielement solute systems were evaluated in columns packed with sand coated with colloidal humic acid–goethite, which has been proposed as a reactive material for in situ remediation of contaminated groundwater (Bianco et al., 2017; Montalvo et al., 2018; Tiraferrri et al., 2017). The PHREEQC geochemical software version 3.4 (Parkhurst and Appelo, 2013) was used to predict by forward modeling the sorption and transport of As(V), Cd, Cu, Ni, and Zn applied in a multielement solution scenario. The coupled model one-dimensional advective and reactive transport of metal(loid)s provides a better understanding of the processes that are expected in the field after the application of this technology.

**Materials and Methods**

**Preparation of Quartz Sand Coated with Colloidal Humic Acid–Goethite**

The colloidal humic acid–goethite (HA-Goe) suspension used in this study was synthesized according to the method of Meckenstock and Bosch (2014) and provided by the University of Duisburg-Essen. This colloidal material has been particularly developed for subsurface injection. A detailed description of the physicochemical characterization of the stock suspension of HA-Goe colloids has been presented elsewhere (Montalvo et al., 2018). Briefly, the stock suspension of colloidal material consisted of nanosized crystallite needles arranged in aggregates with a broad size distribution. Due to the small size of the single goethite crystallites, the material had a very high surface area (202.4 ± 0.3 m$^2$ g$^{-1}$). The net surface charge of the HA-Goe colloids was negative (~37 ± 4 mV) at pH 7.3, which is associated with the coating of humic acids that is used to enhance colloidal stability. The stock suspension contained 66.4 g Fe L$^{-1}$ and 11.2 g organic C L$^{-1}$.

For the column experiment, quartz sand (Dorsilit 8, grain size 0.3–0.8 mm, silica [SiO$_2$] 97.9% by weight, 23 ± 4 µg Fe g$^{-1}$ sand) was coated with a suspension of HA-Goe following a method by Scheidegger et al. (1993) that favors the deposition of HA-Goe colloids on the sand. Prior to coating of the sand with HA-Goe colloids, the quartz sand was heated at 600°C in a muffle furnace for 2 h to remove any organic residues; thereafter it was acid washed overnight (1 M HCl), rinsed with deionized water to neutral pH,
and oven dried. This pretreatment was necessary to make the sand inert to metal cations and serve only as supportive material for the HA-Goe colloids. The HA-Goe-coated sand had an Fe content of 1.35 ± 0.08 mg g⁻¹ determined by inductively coupled plasma optical emission spectrometry (Thermo Scientific ICAP 7400 Duo) after aqua regia (1:3 HNO₃/HCl) extraction.

**Distribution Coefficients of Divalent Metal Cations and Oxygenian**

Two independent batch adsorption experiments, at two pH values, were conducted to investigate the simultaneous adsorption of As(V), Cd, Cu, Ni, and Zn to either colloidal HA-Goe or to HA-Goe-coated sand. In the first batch experiment with the colloids only, 4 mL of HA-Goe suspensions (1.1 g goethite L⁻¹) were placed into bags of dialysis membranes (12–14 kDa) and equilibrated by end-over-end shaking for 72 h with 20 mL of multielement [As(V), Cd, Cu, Ni, and Zn] solutions of increasing initial concentrations (10, 20, and 60 μM of each element). Previous sorption experiments with As(V) and Zn showed that 72 h was sufficient time to obtain equilibrium solution concentrations (data not shown). The multielement solutions were prepared in a background electrolyte solution of 5 mM CaCl₂ and 2 mM 2-(N-morpholino)ethanesulfonic acid (MES buffer, pH 6.1) or 3-(N-morpholino)propanesulfonic acid (MOPS buffer, pH 7.0). After the equilibration time, a subsample of the contact solution was acidified (1% HNO₃) and the total concentration of As, Cd, Cu, Ni, and Zn measured by inductively coupled plasma mass spectrometry (ICP–MS, Agilent 7700).

For the second experiment with coated sand, 2 g of HA-Goe-coated sand was placed into dialysis membrane bags (12–14 kDa) and was equilibrated (72 h) with 20 mL of a multielement solution. The dialysis membrane was used for phase separation, since in previous tests some detachment of colloidal HA-Goe from the sand was observed during end-over-end shaking. The multielement solution contained 18 μM As(V), 32 μM Cd, 18 μM Cu, 18 μM Ni, and 19 μM Zn. The equilibrating solution also contained 5 mM CaCl₂ and 2 mM MOPS pH 7.0. An additional control treatment (sand without HA-Goe colloid coating, i.e., blank sand treatment) was included to determine any adsorption of metalloid contaminants on the substrate material. All adsorption experiments were conducted in duplicate except for sand coated with HA-Goe, for which quadruplicate samples were included.

**Column Experiments**

Column experiments were conducted to evaluate the adsorption and transport of As(V), Cd, Cu, Ni, and Zn applied in single, binary, and multielement systems to HA-Goe-coated sand. Column experiments (10 columns in total) were run in duplicate for each of the following five treatments: (i) As alone, (ii) Zn alone, (iii) As and Zn, (iv) As, Cd, Cu, Ni, and Zn, and (v) natural contaminated groundwater. Glass columns (2-cm diameter, 12-cm length) were filled with 51 g of dry HA-Goe-coated sand by wet packing to prevent air entrapment; small amounts of sand (~5 g) were added while slowly injecting 5 mM CaCl₂ from the bottom of the column. During sand filling, the columns were gently tapped to facilitate homogeneous distribution of the sand and avoid sand layering. The bulk density of the packed sand was 1.35 g cm⁻³. Glass filters (pore size 160–250 μm) were used at the column inlet and outlet to prevent sand loss and for even distribution of the influent solution. After packing, the columns were leached from the bottom with a background solution containing 5 mM CaCl₂ and 0.5 mM MES buffer at pH 6.0 to equilibrate the system. Synthetic and natural contaminated waters were injected at a Darcy velocity of 0.69 cm h⁻¹. The concentration of metal(loids) in the synthetic contaminated water applied as single, binary, or multielement solutions was 66, 47, 4, 39, and 3 μM for As(V), Zn, Cd, Cu, and Ni, respectively. The synthetic contaminated solutions were also prepared in 5 mM CaCl₂ and 0.5 mM MES pH 6.0. Calculations with Visual MINTEQ 3.1 confirmed that no precipitated phases are formed at solution pH 6. The contaminated groundwater was collected at the Barreiro industrial site, Lisbon, Portugal, and contained 99, 0.25, 1.30, 0.09, and 0.22 μM for Zn, Cd, Co, Cu, and Ni, respectively. Additionally, the contaminated groundwater contained the following macroelements: 15 mM Ca, 5.8 mM Na, and 1 mM Mg and the pH of the water was 7.65. The synthetic contaminated solutions and groundwater were injected for 57 pore volumes (PVs). Thereafter, the columns were flushed with the background solution (5 mM CaCl₂ and 0.5 mM MES pH 6.0) until tailing of the BTCs was well established and the outflow concentrations approached baseline levels, which in this study were considered to be C/C₀ ≤ 0.1. Effluent samples were manually collected in polyethylene tubes every 1 or 2 PVs during the injection of contaminated solutions and, after the solutions were switched to background, samples were collected every 2 or 3 PVs. Leachates were acidified to 1% HNO₃ and the total concentration of As, Cd, Cu, Ni, and Zn was measured by ICP–MS. No mobilization of goethite was observed during the experiments, as evidenced by the clear solutions collected in the effluent with measured Fe concentrations close or below the limit of detection (0.3 μg L⁻¹). The transport of Br⁻, a non-sorbing ion, was investigated to estimate the longitudinal dispersivity (λ) of the HA-Goe packed columns. A pulse (0.3 PV; 15.2 mL = 1 PV) of 0.2 mM Br⁻ was injected and the effluent samples analyzed by ion chromatography ( Dionex ICS-2000 with an AS17-C column). The Br⁻ tracer test was conducted before the metalloid transport experiments. At the end of the experiment, columns were dismantled and HA-Goe-coated sand retrieved. The HA-Goe-coated sand from each column was homogenized and air dried; three subsamples were taken and digested in aqua regia to determine total As, Cd, Cu, Ni, and Zn concentrations.

**Statistical Analysis**

One-way analysis of variance was performed for each contaminant by pH with the JMP statistical package version 14.0 (SAS Institute) to assess differences in the distribution coefficients at different initial molar concentrations of each element in HA-Goe.
colloidal suspension. Analysis of variance for As(V) and Zn was also conducted for column data from single, binary, and multielement systems to determine differences in retardation factors and the percentage of the element sorbed. Differences between treatments were analyzed with the Tukey test and considered significant at the $P \leq 0.05$ level.

Results and Discussion

Batch Sorption Experiment

Contaminant Distribution Coefficients and Ion Selectivity

Distribution coefficients ($K_d$) were calculated for each metal or metalloid contaminant to assess the effect of initial ion concentration on the adsorption efficiency by colloidal HA-Goe. The $K_d$ expressed as the ratio of the adsorbate on the solid phase to that in solution represents the adsorption affinity of the metal or metalloid for the adsorbent (HA-Goe):

$$K_d = \frac{M_s}{[M]}$$

where $M_s$ is the amount of adsorbate retained in the solid phase (mg kg$^{-1}$), and $[M]$ is the total concentration of adsorbate remaining in solution (mg L$^{-1}$). For the multielement solution systems investigated at the two solution pH levels, the ion selectivity sequence followed the order: As(V) $\sim$ Cu $> >$ Zn $>$ Cd $>$ Ni. This trend is in agreement with studies that investigated competition between divalent metal cations on goethite (Cu $>$ Zn $>$ Cd $>$ Co $>$ Ni) (Christophi and Axe, 2000; Forbes et al., 1976). For each metal cation (Cd, Cu, Ni, and Zn) and metalloid [As(V)], the $K_d$ values decrease with increasing total initial ion concentration as sorption sites become saturated (Table 1). In general, As(V) and Cu presented the highest $K_d$ values, showing that these are the contaminants that are most strongly retained and, hence, with higher affinity for HA-Goe. The metals with the lowest $K_d$ values were Cd and Ni, indicating that these two elements can be readily exchanged by more strongly sorbing Zn and Cu.

The effect of solution pH on the adsorption of heavy metals to goethite is well known and extensively documented (Forbes et al., 1976). In general, adsorption of cations increases with increasing pH. Larger metal $K_d$ values were found at pH 7.0 than at pH 6.1. The effect of pH was more evident at the lowest contaminant concentration (10 $\mu$M), at which distribution coefficients increased up to sevenfold by increasing the pH by one unit (Table 1, e.g., Zn log$_{10}$ $K_d = 4.23$ at pH 6.1 vs. 5.08 at pH 7.0). Conversely, the adsorption of anions slightly decreased with increasing pH; that difference was statistically significant ($P < 0.05$) only at the concentrations of 10 and 20 $\mu$M. The $K_d$ of As(V) at the initial concentration of 10 $\mu$M was nearly two times lower at pH 7 than at pH 6.1 (Table 1). At pH values that are below the point of zero charge for goethite ($p\text{H}_{ZPH}$ 6.9), the adsorption of As(V) can be promoted as the surface of goethite becomes more positively charged, and at that pH, negatively charged As(V) species are predominant ($\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$) (Mamindy-Pajany et al., 2011).

Contaminant Adsorption to Humic Acid–Goethite-Coated Sand

In this study, quartz sand was coated with colloidal HA-Goe to mimic the deposition and immobilization of HA-Goe colloids on the substrate after injection in contaminated subsurface waters. The calculated sorption $K_d$ values of metals and the metalloid on such prepared sand are shown in Table 2. The ranking among elements was similar to that for the original colloids, i.e., As $\sim$ Cu $> >$ Zn $>$ Cd $~$ Ni. The adsorption of contaminants to uncoated sand (blank sand) was negligible (<5%), validating its main function as a support material for the HA-Goe colloids.

General Column Transport Parameters

The general column transport parameters were used to estimate the absence of physical nonequilibrium in the system (i.e., ideal transport behavior) (Pang et al., 2002). The average effective porosity of the sand was 0.40 ± 0.01 and the water residence time in the column was 7.0 h.

![Table 1. Distribution coefficients ($K_d$) for As, Cd, Cu, Ni, and Zn applied as a mixture at different initial molar concentrations of each element in humic acid–goethite (HA-Goe) suspensions (1.1 g goethite L$^{-1}$) and different solution pH values that were constant.](image)

<table>
<thead>
<tr>
<th>Conc. added $\mu$M</th>
<th>pH</th>
<th>$\log_{10}K_d$</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.1</td>
<td>6.37 ± 0.04</td>
<td>3.76 a</td>
<td>3.56 a</td>
<td>4.23 a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>5.69 b</td>
<td>3.61 b</td>
<td>3.43 b</td>
<td>3.94 b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>4.11 c</td>
<td>3.34 c</td>
<td>3.19 c</td>
<td>3.55 c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>7.0</td>
<td>6.08 a</td>
<td>4.21 a</td>
<td>4.11 a</td>
<td>5.08 a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>5.43 b</td>
<td>3.95 b</td>
<td>3.80 b</td>
<td>4.68 b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>4.05 c</td>
<td>3.55 c</td>
<td>3.37 c</td>
<td>4.07 c</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Different letters indicate significant difference ($P \leq 0.05$) within each column per pH chosen (Tukey test on log-transformed $K_d$ values).

![Table 2. Distribution coefficients ($K_d$) with standard error of quadruplicates for humic acid–goethite (HA-Goe) coated sand and duplicates for uncoated sand in parentheses for As, Cd, Cu, Ni, and Zn adsorbed to HA-Goe coated sand and uncoated sand (blank sand).](image)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$K_d$ with standard error of quadruplicates</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated sand</td>
<td>6100 (400) 47 (4)</td>
<td>5900 (400) 44 (1)</td>
<td>1800 (500)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uncoated sand</td>
<td>2.0 (0.22) 0.8 (0.08)</td>
<td>135 (7.58) 1.8 (0.001)</td>
<td>5.2 (0.06)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Transport of Arsenate and Zinc in Single, Binary, and Multielement Solute Systems

In this study, the BTCs are expressed as relative concentrations \( \frac{C}{C_0} \) vs. PVs, where \( C \) represents the concentration of contaminants in the effluents and \( C_0 \) the concentration of contaminants in the inlet solution. As shown in Fig. 1, the shape of the BTCs for As(V) and Zn applied in single, binary, and multielement solute systems are asymmetrical and exhibit tailing. This shape of BTC is suggestive of rate-limited (i.e., nonequilibrium adsorption–desorption) and/or nonlinear adsorption reactions (i.e., lower adsorbent–adsorptive affinity at higher concentrations) during transport (Barnett et al., 2000; Brusseau et al., 1989). Similar transport features for As(V) and Zn were previously reported in soils, and in those studies breakthrough data were better simulated by nonequilibrium transport models (Darland and Inskeep, 1997; Selim et al., 2013). Since the transport of a non-sorbing tracer (Br\(^-\)) was well described with the equilibrium convection–dispersion equation (see above), it is likely that the asymmetric shape of the BTCs was due to chemical nonequilibrium conditions (rate-limited adsorption), given also the relative short residence time in the columns (7 h).

The BTCs are shown in Fig. 1, with statistical analysis in Table 3. In single-element columns, the BTC for Zn reached a peak concentration that was nearly equivalent to complete saturation \( \frac{C}{C_0} = 0.95 \) after the pulse injection (57 PVs) of Zn-contaminated water. During desorption (injection of Zn-free solution), the Zn concentration in the effluents slowly decreased with time and exhibited tailing. Based on the integration of the BTCs, it was calculated that about 59% of the added Zn was irreversibly adsorbed on the HA-Goe-coated sand. In contrast, the BTCs for As(V) showed a more gradual increase of the leachate concentrations (less sharp front) than that of Zn and also reached a lower concentration maximum \( \frac{C}{C_0} = 0.68 \) after the pulse injection. Additionally, it was estimated that 69% of the added As(V) was retained in the column. This finding supports the results of the batch experiments in that As(V) is more strongly retained than Zn and suggests that the adsorbent (HA-Goe colloids) could be a suitable material for remediation of As(V)-contaminated water due to its higher adsorption affinity.

In the binary systems, the BTC for Zn indicates that the presence of As(V) enhanced Zn adsorption (synergism), i.e., the Zn \( \frac{C}{C_0} \) decreased compared with Zn only (Table 3). Conversely, the effect of Zn on the breakthrough of As(V) was small and even antagonistic as evaluated from the peak As \( \frac{C}{C_0} \). The As(V)-induced adsorption of Zn is not unexpected (Gräfe et al., 2004) and agrees with previous work. In a recent study, Kim et al. (2016) evaluated the co-transport of As(V), Cd, and Zn in columns packed with an uncontaminated clay loam soil (pH 7.21). Results from the transport experiment showed that in the cation–oxyanion systems, the retention of either Cd or Zn was greatly enhanced (e.g., the retention factor for Zn increased 2.4-fold compared with Zn applied singly) but that the retention of As(V) was mostly unaffected (Kim et al., 2016). The plausible reasons for enhanced adsorption of cations (Zn\(^{2+}\), Cd\(^{2+}\)) by the specific adsorption of As(V) to goethite have been adduced to (i) electrostatic effects, i.e., As(V) increases the negative surface charge of goethite inducing electrostatic adsorption of cations, and (ii) the formation of arsenate-bridged ternary complexes \((=\text{Fe}–\text{As}–\text{Cd})\) (Jiang et al., 2013).

In this study, we did not observe an effect of Zn on the adsorption of As(V), and the reason may be that the concentrations in solution were not high enough for co-precipitation reactions. For example, Jiang et al. (2013) reported that Cd enhanced the sorption of As(V) only at high initial concentrations that would cause the formation of co-precipitates.

The BTC results from the multielement treatment compared with the corresponding single-element BTCs showed a synergistic effect of cationic metals on the reactive transport of As (i.e., more sorption, less leaching) and an antagonistic effect of the cations
Table 3. Breakthrough data of As and Zn after injection of 57 pore volumes (PV) that corresponds to 399 h of different influents with single elements or mixtures in a 5 mM CaCl₂ background. The retardation factor ($R$) was calculated from the sorption coefficient ($K_d$) obtained by inverse fitting the two-site linear sorption chemical nonequilibrium transport model in HYDRUS (Šimůnek and van Genuchten, 2008) to As(V) and Zn breakthrough curves (BTCs). The parameters $f$ and $\alpha$ were also obtained by fitting the BTCs.

<table>
<thead>
<tr>
<th>Influent</th>
<th>As $R$†</th>
<th>$f$‡</th>
<th>$\alpha$§</th>
<th>$C/C_d$ at 57 PV</th>
<th>Amount sorbed after 57 PV</th>
<th>Zn $R$</th>
<th>$f$</th>
<th>$\alpha$</th>
<th>$C/C_d$ at 57 PV</th>
<th>Amount sorbed after 57 PV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single As (66 μM As)</td>
<td>58 b#</td>
<td>0.30</td>
<td>0.140</td>
<td>0.68 b</td>
<td>77 b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single Zn (47 μM Zn)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>53 a</td>
<td>0.65</td>
<td>0.038</td>
<td>0.90 a</td>
<td>78 ab</td>
</tr>
<tr>
<td>Binary mixture (66 μM As, 47 μM Zn)</td>
<td>43 b</td>
<td>0.07</td>
<td>0.970</td>
<td>0.76 a</td>
<td>77 b</td>
<td>82 a</td>
<td>0.56</td>
<td>0.049</td>
<td>0.75 b</td>
<td>85 a</td>
</tr>
<tr>
<td>Multi-element (66 μM As, 47 μM Zn, 39 μM Cu, 4 μM Cd, 3 μM Ni)</td>
<td>90 a</td>
<td>0.47</td>
<td>0.069</td>
<td>0.51 c</td>
<td>90 a</td>
<td>70 a</td>
<td>0.52</td>
<td>0.005</td>
<td>0.96 a</td>
<td>72 b</td>
</tr>
</tbody>
</table>

† Retardation factor, $R = 1 + K_d \rho / \theta$, where $K_d$ is the sorption coefficient, $\rho$ is the bulk density, and $\theta$ is the porosity.
‡ Fraction of equilibrium sites.
§ First-order kinetic rate constant.
¶ Relative concentration.
# Data are means of two columns, significant differences in data within each column are indicated by different letters ($P < 0.05$; Tukey test).

on the transport of Zn. The contrasting effects are indicative of (i) competition between Zn and the other divalent cations, particularly Cu, which showed more affinity for HA-Goe-sand (Tables 1 and 2); and (ii) likely synergistic adsorption between As(V) and Cu. As described below, Cu was the most strongly adsorbed cation to HA-Goe-sand as no breakthrough of Cu was observed within the time of investigation, even after introducing contaminant-free solution that promotes desorption. The strong adsorption of Cu might have rendered the surface of the adsorbent (HA-Goe-coated sand) more positively charged, thus increasing the electrostatic attraction for the negatively charged oxyanion. Nelson et al. (2013) showed from stoichiometric analysis from co-adsorption experiments of Cu and As(V) on goethite that the ternary surface complex $\text{[Fe}_3\text{OFeOH)}\text{Cu}_2\text{(OH)}_2\text{HASO}_4^-$ in which As(V) binds to goethite by coordinating to specifically adsorbed Cu is largely present at a wider pH range (4–9).

The transport of sorbing solutes is usually quantitatively characterized by the retardation factor ($R$), which is an important parameter in the convection–dispersion model. For sorbing solutes, $R$ values are >1. This means that the solute moves at an effective velocity that is lower than that of the fluid itself. Here, $R$ values were used to better compare the relative sorption of As(V) and Zn in single, binary, and multielement systems on HA-Goe-coated sand. The retardation factor was derived from the sorption parameter ($K_d$) obtained by inverse fitting of the two-site chemical nonequilibrium model with linear sorption from HYDRUS (Šimůnek et al., 2005) to the adsorption part of the BTCs. The parameters that describe nonequilibrium sorption ($f$, the fraction of equilibrium sites, and $\alpha$, the first-order kinetic rate constant) in the two-site model were also obtained by inverse fitting (Table 3). In general, $R$ values were higher for As(V) than for Zn (except in the binary solute system), which agrees with the higher affinity of HA-Goe-coated sand to adsorb As(V) as reflected from batch sorption tests (Tables 1 and 2). The $R$ value for As(V) was higher (i.e., enhanced adsorption) in the multielement system than in the single-element columns, probably due to the Cu–As synergistic sorption reactions, as discussed above. Similarly, Zn–As synergism probably explains the high $R$ value for Zn in the binary system compared with Zn added singly or with other competing cations in the multielement system.

**Competitive Divalent Metal Cation Transport in Columns**

Figure 2 displays the transport of As, Cd, Cu, Ni, and Zn injected in multielement solution. The concentrations of Cd and Ni in the effluent solution exceeded by nearly 50% the respective inlet concentrations after 40 PVs of continuous injection of the contaminated solution. This distinctive overshooting phenomenon suggests competition of Cd and Ni for sorption sites with the more strongly sorbing cations Cu and Zn. As more sorption sites became occupied, previously adsorbed Cd and Ni were probably desorbed by the subsequent adsorption of the cations with higher affinity for HA-Goe, hence generating the overshoot. This characteristic behavior during competitive transport was previously reported for Cu and Cd in soil-packed columns, where the overshoot of Cd exceeded by 10% the initial Cd concentration (Tsang and Lo, 2006). Overall, the degree of retardation of the contaminants in the column agreed with the sorption affinity observed in batch experiments, i.e., As(V) and Cu are preferentially adsorbed to HA-Goe colloids over Zn, Cd, and Ni. The ranked affinity of the selected contaminants for HA-Goe coated sand is: As $\sim$ Cu $>>$ Zn $> Cd \sim Ni.

The results from the columns that received natural contaminated groundwater are presented in Fig. 3. The metals of concern in this groundwater were Zn and Cd, both elements with concentrations that would merit remediation. The measured Zn and Cd concentrations in the leachates collected after the passage of 57 PVs of groundwater were all well below the threshold values for
Zn and Cd (i.e., <30 μg Zn L−1 and <1 μg Cd L−1), suggesting an efficient immobilization of the contaminants in the column. This enhanced retention of Zn and Cd compared with the other treatments is related to the higher pH of the groundwater (7.6 vs. 6.1 for the other influents).

**Modeling Sorption and Transport of Arsenate, Cadmium, Copper, Nickel, and Zinc**

Column transport experiments were conducted to identify antagonistic and synergistic interactions among the relevant cationic and anionic contaminants and their implications for the remediation of contaminated water. In this study, the forward modeling approach with PHREEQC was used to evaluate the role of competitive and synergistic adsorption on the mobility of As(V), Cd, Cu, Ni, and Zn. The models selected for the simulation were surface complexation on hydrous ferric oxide (HFO) (Dzombak and Morel, 1990) and Windermere’s humic acid model (WHAM) (Tipping and Hurley, 1992). The databases waterqf.dat and T&H.dat that contain cation and humic acid reactions were used for the calculations. The HFO model simulates cation and anion adsorption on the surface of Fe oxide and assumes weak (0.2 mol weak site mol−1 HFO) and strong (0.005 mol strong site mol−1 HFO) binding sites. The WHAM model accounts for the interaction between cations and humic acids and specifies that the complexing sites are distributed over carboxylic and phenolic groups, each given a charge. The number of binding sites for HFO and humic acid are the adjustable parameters in the model. The binding sites for HFO were estimated by fitting these to the experimental batch $K_d$ value of the coated sand (data of Table 2) for As(V) only. The best fit [i.e., observed vs. predicted $K_d$ value for As(V) differ by a factor of 1.0 ± 0.1] was obtained when only 25% of the goethite was considered reactive, which led to $1.2 \times 10^{-4}$ mol weak sites and $0.3 \times 10^{-5}$ mol strong binding sites for the model (Supplemental Fig. S1). The model was further adjusted by estimating the contribution of humic acids to the adsorption of cations. Binding sites were estimated by fitting these to the batch $K_d$ value for Cu only due to the highest affinity for natural organic matter. This two-point calibration of the model also adequately predicted the sorption of other elements (Cd, Ni) on the coated sand but not the sorption of Zn, for which the $K_d$ value was 10-fold higher than predicted, potentially because of the Zn–As synergistic interactions that are not included in the models used here (Supplemental Fig. S1).

The geochemical model was then coupled with one-dimensional advective transport to simulate the transport of As(V), Cd, Cu, Ni, and Zn in the multielement solution. The pH was set to 7.25, which is the pH recorded in the effluent solution during the first 30 PVs. For the simulation, an extended injection time (59 d)
for the contaminated solution was used to determine any possible breakthrough of Cu, which was not observed during the experiment. The combined general surface complexation model HFO and the WHAM model coupled with one-dimensional transport assembled in PHREEQC code was able to correctly capture the most essential features of the BTCs, including competition effects and the order in which the contaminants broke through. The transport of Cd, Ni, and Zn were well captured by the model, including the overshooting of Cd and Ni due to competition for sorption sites albeit that the model predicted higher concentrations in the effluent. Modeled BTCs in Fig. 2 showed that As(V) and Cu are strongly adsorbed to HA-Goe-coated sand, with BTCs initiating at about 120 and 180 PVs, respectively. The difference in the breakthrough time for As(V) between the model predictions and experimental data can be explained by chemical nonequilibrium during the transport of As(V), which could have been present in the columns but is not considered in the PHREEQC reactive transport model. The geochemical model is based solely on chemical equilibrium sorption reactions. For Cd, Ni, and Zn, the model predicted twofold earlier breakthrough times. For example, at C/C₀ = 0.5, the modeled breakthrough for Zn, Ni, and Cd occurred at approximately 20, 18, and 15 PVs, whereas the observed breakthroughs were at about 40 PVs for Zn, 32 PVs for Ni, and 33 PVs for Cd.

Under the conditions of the column experiment that received the multielement solution, the model predicted that about 78 mg As(V) g⁻¹ HA-Goe can be adsorbed before the maximum concentration limit of 10 μg As L⁻¹ in water is exceeded. In other words, about 116 PVs of the contaminated water can be filtered before the outlet concentration of As exceeds the limit. For Cd and Ni, <1 mg g⁻¹ HA-Goe is the estimated sorption capacity before the maximum concentration limits are exceeded (the limit for Cd is 5 μg L⁻¹ and for Ni it is 20 μg L⁻¹ in Belgium); and these sorption maxima correspond to 14 PVs for Cd and 18 PVs for Ni. Meanwhile for Zn and Cu the estimated sorption capacities are 9 and 51 mg g⁻¹ HA-Goe, respectively (the limit for Zn is 200 μg L⁻¹ and for Cu it is 100 μg L⁻¹ in Belgium); these correspond to 21 PVs for Zn and 170 PVs for Cu.

Because the adsorption of metals on HA-Goe depends strongly on the pH of the solution, BTCs for the contaminants in the multielement solution were also simulated at pH 6 (data not shown). The model predicted that at about 4 PVs of injection of the contaminated solution, the divalent cations Cd, Ni, and Zn would have already reached their breakthrough (C/C₀ = 1). For Cu, the concentration in the leachates may have surpassed the limit only after 14 PVs of groundwater. At this solution pH, the model also predicted that As(V) is less mobile (BTC initiates after 150 PVs), which is in agreement with the batch data [i.e., larger Kₐd values for As(V) at pH 6 than at pH 7].


