Groundwater Arsenic Adsorption on Granular TiO_2 : Integrating Atomic Structure, Filtration, and Health Impact

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S Supporting Information

ABSTRACT: A pressing challenge in arsenic (As) adsorptive filtration is to decipher how the As atomic surface structure obtained in the laboratory can be used to accurately predict the field filtration cycle. The motivation of this study was therefore to integrate molecular level As adsorption mechanisms and capacities to predict effluent As from granular TiO_2 columns in the field as well as its health impacts. Approximately 2,955 bed volumes of groundwater with an average of $542 \mu\text{g/L}$ As were filtered before the effluent As concentration exceeded $10 \mu\text{g/L}$, corresponding to an adsorption capacity of $1.53 \text{ mg As/g TiO}_2$. After regeneration, the TiO_2 column could treat 2,563 bed volumes of groundwater, resulting in an As load of 1.36 mg/g TiO_2 . Column filtration and EXAFS results showed that among coexisting ions present in groundwater, only Ca^{2+} , $\text{Si}(\text{OH})_4$, and HCO_3^- would interfere with As adsorption. The compound effects of coexisting ions and molecular level structural information were incorporated in the PHREEQC program to satisfactorily predict the As breakthrough curves. The total urinary As concentration from four volunteers of local residences, ranging from 972 to $2,080 \mu\text{g/L}$ before groundwater treatment, decreased to the range $31.7\text{--}73.3 \mu\text{g/L}$ at the end of the experimental cycle (15–33 days).

INTRODUCTION

Adsorptive filtration is one of the most cost-effective and user-friendly techniques to provide arsenic (As) safe drinking water in geogenic As contaminated areas.^{1,2} Integration of mounting molecular-level evidence over the past decade has shown that the mechanism of As adsorption mainly involves the formation of bidentate binuclear inner sphere surface complexes.^{3–5} Although substantial progress has improved our understanding of batch and field filtration experiments, a pressing challenge is to decipher how the molecular-level mechanism obtained in the laboratory can be used to accurately predict the field filtration cycle.

Rethinking the failure in prediction of field filtration breakthrough curves using parameters obtained with batch experiments, we realized that the adsorption kinetics might not be the critical contributor, as initially thought. The difference in reaction kinetics between batch complete-mixed and column flow-through conditions has long been recognized and solved by incorporating a nonequilibrium kinetics block in simulation code such as PHREEQC.^{6,7} On the other hand, even without the kinetics block, the adsorptive filtration of As(III) in synthetic water matrices through iron-oxide-coated rock can be successfully modeled.⁸ This success may be attributed to instantaneous uptake of As by most metal oxides. However, a real difficulty surfaces when predicting the groundwater As breakthrough curves in field columns, even with the kinetics

block and additional As adsorption reactions.^{8,9} The compound effects of groundwater matrices on As adsorption cannot be overstated.

Groundwater As adsorption on metal oxides can be suppressed or enhanced in the presence of coexisting ions. Previous studies demonstrated that some anions such as phosphate and silicate could strongly compete with As adsorption,¹⁰ whereas others including sulfate, nitrate, and chloride only have negligible effects.¹⁰ The complexity of the coexisting ion effect can be manifested by bicarbonate, which competes weakly with As adsorption, and may greatly promote the release of adsorbed As in the presence of calcium and magnesium.¹¹ In contrast to anions, cations such as calcium and magnesium have synergistic effects on As adsorption due to electrostatic forces.⁹ Although much is known about the interference of single ions, little is understood about their compound impacts on As adsorption and transport during field column studies. In particular, uncertainties about molecular surface complexes in the presence of coexisting ions during filtration may contribute to the failure of the geochemical transport model using batch parameters.¹²

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The adsorption and mobility of As are greatly influenced by its speciation. The more toxic and mobile As(III) in groundwater can be readily oxidized to As(V) upon exposure to air.¹³ Moreover, As(III) adsorbed on Fe(III) and Mn(IV) oxides could be oxidized, which may alter the As mobility and adsorption capacity.^{14,15} Therefore, As speciation and redox transformation should be considered in evaluating the long-term filtration process.

Removal of As from drinking water is beneficial to human health. However, case studies have rarely reported how long it takes for the As concentration in biomarkers such as urinary As to decrease upon As removal. The difficulty in finding such volunteers who drink the same groundwater matrices except for the existence of As may be the reason for the lack of this kinetics information. This critical knowledge, nevertheless, is essential to understand the impact of As removal on human health.

The objective of this study was to integrate molecular level As adsorption mechanisms and capacities to predict field column As filtration and its health impacts. Granular titanium dioxide (TiO₂) was used as the adsorbent due to its effectiveness in remediation of As in groundwater and wastewater.^{9,16} The compound effects of coexisting ions were investigated using column filtration experiments and extended X-ray absorption fine structure (EXAFS) spectroscopy. Such molecular level structural information was incorporated in the PHREEQC program to predict the As adsorptive filtration breakthrough curves. The change in urinary As concentration and speciation were monitored in local residents as an indicator of health impact.

MATERIALS AND METHODS

Experimental Site. A representative groundwater well in the Datong Basin, China (39°35' N latitude and 112°85' E longitude) was selected. Our previous study showed that the As concentration ranged from <1 to 1,160 µg/L (0–0.015 mmol/L) in the Datong Basin.¹⁷ The average As concentration in the selected groundwater was 454 µg/L (0.006 mmol/L) As(III) and 88 µg/L (0.001 mmol/L) As(V) at pH 8.2–8.4. The groundwater in Datong Basin is slightly alkaline and of the NaHCO₃ type.¹⁷ The detailed groundwater parameters are listed in Table S1.

Materials. Stock solutions of 1,000 mg/L (13.348 mmol/L) As(III) and As(V) were prepared by dissolving NaAsO₂ and Na₃AsO₄·12H₂O in deionized (DI) water, respectively. To prevent As(III) oxidation and CO₂ contamination, DI water was purged with nitrogen for at least an hour. The nanocrystalline TiO₂ was prepared by hydrolysis of titanyl sulfate at 4 °C. Then, TiO₂ was granulated to 60–80 mesh size using our reported method.¹⁶ The BET surface area of the granular TiO₂ was 196 m²/g, the site density was 6 mmol/g, and the point of zero charge was 5.8.¹⁸

Batch Adsorption Isotherms. Adsorption isotherm experiments were performed to determine the As(III) and As(V) adsorption capacity on granular TiO₂ under groundwater solution chemistry at pH 8.2. Suspension samples containing 1 g/L TiO₂ and 1–800 mg/L (0.013–10.667 mmol/L) As(III) or As(V) at pH 8.2 in 0.04 M NaClO₄ were mixed on a rotator for 72 h in the dark. Then, the samples were passed through a 0.45-µm membrane filter for soluble As measurements.

Field Filtration Experiments. The adsorptive filtration studies were performed using a small filter house for process

analysis and a large one to generate enough water for drinking. The small (large) column with an inside diameter of 1.1 (7.7) cm was filled with 10 (750) g of granular TiO₂, resulting in a bed volume of 9.5 (850) mL. The empty bed contact time (EBCT) for both small and large columns was set to 4 min. To prevent suspended solids from flowing into the filter house, a sediment filter with a 5 mm cartridge was installed in front of the TiO₂ column covered with aluminum foil. A trace amount of dissolved oxygen (<0.8 mg/L) existed in the groundwater.

The effluent samples from the small column were collected every 2 h for As concentration and speciation analysis on site. The effluent samples from the large column were collected twice a day. The alkalinity of groundwater before and after filtration was also analyzed with the titration method. After the column experiments finished, samples were brought to the lab to analyze major cations and anions.

Urine Sample Collection. The urine samples were collected with written consents in accordance with the regulations of the Institutional Committee at the Research Center for Eco-Environmental Sciences and the Chinese Ethics Committee of Registering Clinical Trials (ChiECRCT-20150036). The first morning void urine samples were collected from four volunteers in the well owner's family who were drinking treated groundwater. Among the four volunteers, the owner (male, age 56), his wife (age 50), and their daughter (age 26) have used the groundwater for more than 30 years. A visitor to their family (male, 29) moved in 2 weeks before and had never used As-tainted water before. Thus, the study included long- and short-term As exposure cases. The urine samples were stored at 4 °C until analysis.

Sample Analysis. Concentrations of As(III), As(V), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) in water and urine samples were determined by a high performance liquid chromatography atomic fluorescence spectrometer (HPLC-AFS, Haiguang, China) on site. The detection limits for the four As species were 0.7 µg/L for As(III), 1.3 µg/L for DMA, 1.5 µg/L for MMA, and 1.7 µg/L for As(V),¹⁹ and the detailed procedures are shown in the Supporting Information (SI). The anions (with detection limit, mg/L) including F[−] (0.013), Cl[−] (0.014), NO₂[−] (0.013), SO₄^{2−} (0.032), Br[−] (0.024), NO₃[−] (0.012), and PO₄^{3−} (0.019) were measured using a DX-1100 ion chromatograph (Dionex, US) with an AS11-HC column.²⁰ Common cations (with detection limit, mg/L) such as Ca²⁺ (0.01), Mg²⁺ (0.002), Na⁺ (0.2), K⁺ (0.5), Fe³⁺ (0.03), Ti⁴⁺ (0.005), Si(OH)₄ (0.01), and Mn²⁺ (0.01) were analyzed by inductively coupled-plasma optical emission spectroscopy (ICP-OES, PerkinElmer, US).

The As *K*-edge (11,867 eV) EXAFS spectra of spent TiO₂ samples were collected on beamline 01C1 at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The EXAFS data were collected at 77 K using a helium cryostat to prevent beam-induced oxidation. The data collection and analysis were described in our previous reports^{9,19} and detailed in the SI.

TiO₂ Regeneration. The spent TiO₂ was regenerated with consecutive 2 mol/L NaOH and HCl treatments with a solid/liquid ratio at 1:10. NaOH solution (2 mol/L) was first passed through the column in a closed-loop flow mode at 2.4 mL/min for 4 h, and the column was then rinsed with treated groundwater until pH became neutral. The second regeneration solution was changed to 2 mol/L HCl. After rinsing, the column could be used for a new filtration cycle.

Surface Complexation and One-Dimensional Transport Modeling. The charge distribution multisite complexation (CD-MUSIC) model was used to describe the adsorption of groundwater As and coexisting ions on TiO_2 . The proton affinity constant was set to the PZC of TiO_2 (5.8), and the adsorption constants of counterions were set to -1 . The charge distribution (CD) value shows the fraction, f , of the charge of the central As ion attributed to the surface plane, and the remaining part ($1-f$) were positioned toward the diffuse layer. The CD was determined by fitting model-calculated values to the experimental data. The calculation was performed using the chemical equilibrium program MINTeq, and the detailed parameters are shown in Table S3 in the SI.

The field filtration was simulated and predicted using the PHREEQC code with the CD-MUSIC model and one-dimensional advective transport. To simulate the 1D transport filtration for the 10-g TiO_2 small column, 4 cells with a length of 0.025 m each were constructed with EBCT of 4 min. Similarly, to predict the filtration results for the 750 g TiO_2 large column, a 4-cell column with a length of 0.051 m each was used. A total of 29,684 shifts were specified with a corresponding time step of 34.2 s.

RESULTS AND DISCUSSION

As Adsorption Capacity. The As adsorption conformed to the Langmuir isotherm (Table S2 and Figure S1), and As(III) adsorption capacity (93.0 mg/g, or 1.241 mmol/g) was much higher than As(V) (35.2 mg/g, 0.470 mmol/g) in simulated groundwater matrices (Figure 1), which may be due to the

Figure 1. Adsorption capacities of As(III) (red) and As(V) (blue) in 0.04 M NaClO_4 at pH 8.2 with 1 g/L TiO_2 . The points are experimental results, and the lines are CD-MUSIC modeling results.

alkaline groundwater condition (pH = 8.2). The As(III) adsorption increases with increasing pH values up to its pK_{a1} (9.3), whereas the adsorption of As(V) dramatically decreases under alkaline conditions, conforming to oxyanion adsorption characteristics.²¹ In line with previous studies, our results show that As(III) adsorption capacity was higher than As(V) under alkaline conditions.²²

The adsorption isotherms could be well described with the CD-MUSIC model (Figure 1). The model included $\text{Ti}_2\text{O}_2\text{AsO}^{-5/3}$ for the As(III) surface complex and $\text{Ti}_2\text{O}_2\text{AsO}_2^{-5/3}$ for As(V) as supported by our previous EXAFS results.²¹ The formation constants ($\log K$) for the inner-sphere As(III) and As(V) complexes were 12.0 and 28.8, respectively (Table S3), which are comparable with previous studies.^{11,23} The satisfactory modeling results endorsed the application of CD-MUSIC in the PHREEQC code to predict As adsorptive transport in the TiO_2 columns.

Field Column Studies. To exploit As adsorptive transport behaviors in TiO_2 filters, a small column with 10 g of TiO_2 was used for treatment of groundwater with an average of 454 $\mu\text{g/L}$ As(III) and 88 $\mu\text{g/L}$ As(V). The As breakthrough curves for the new and regenerated TiO_2 columns are shown in Figure 2. I. The As concentration and speciation in the raw groundwater during the column experiments are shown in Figure S2.

Figure 2. Observed (points) and simulated (lines) As (I), Si(OH)_4 (II), Ca^{2+} (III), and HCO_3^- (IV) breakthrough curves with 10 g of new (red) and regenerated (blue) granular TiO_2 as a function of bed volumes during the filtration experiments. The dashed lines in (I) were PHREEQC modeling results with the inclusion of kinetics module. The average initial As(III) and As(V) concentrations in the groundwater were 454 and 88 $\mu\text{g/L}$, respectively. The EBCT was 4 min, and flow rates were 2.4 mL/min. Q represents the total adsorption capacities during the column filtration experiments, while Q_{10} is the As adsorption capacity when the effluent As concentration $<10 \mu\text{g/L}$.

The TiO_2 column could filter 2,955 bed volumes (BV) of groundwater before the effluent As exceeded 10 $\mu\text{g/L}$, resulting in an adsorption capacity of 1.53 mg As/g TiO_2 (0.020 mmol/g). After the TiO_2 regeneration, another 2,563 BV were treated, corresponding to 1.36 mg As/g TiO_2 (0.018 mmol/g). The slight decrease in As adsorption capacity could be attributed to incomplete regeneration of the TiO_2 surface sites. Nevertheless, the As adsorption capacity in our present study is comparable with previous reports (0.002–1.87 mg/g, Table S4). For example, approximately 45,000 BV of groundwater containing 35–44 $\mu\text{g/L}$ As(V) had been treated, and the As load on TiO_2 was 1.7 mg/g.^{24,25}

With the satisfactory As removal in the 10-g TiO_2 filters, a large column containing 750 g of TiO_2 was used to supply As-free drinking water to the local residents. With the same EBCT as the 10-g small filters (4 min), the large TiO_2 column could pass 2,190 L of groundwater (2,577 BV) before the effluent As exceeded 10 $\mu\text{g/L}$, resulting in an adsorption capacity of 1.49 mg As/g TiO_2 (0.020 mmol/g, Figure 3). After the TiO_2 regeneration, another 2,033 L of groundwater (2,392 BV) was treated, corresponding to 1.38 mg As/g TiO_2 (0.018 mmol/g).

As(III) Oxidation in the Column. As(III) was oxidized during column filtration, because As(V) was the only As species both in the effluent (Figures 2 and 3) and on TiO_2 media as evidenced by our XANES analysis (Figure S3). Influent As(III) may be readily oxidized upon the change of redox potential and during TiO_2 column filtration.²⁶ Such an oxidation of As(III)

Figure 3. Observed (points) and simulated (lines) As breakthrough curves with 750 g of new (red) and regenerated (blue) granular TiO_2 as a function of bed volumes during the filtration experiments. The average initial As(III) and As(V) concentrations in the groundwater were 454 and 88 $\mu\text{g/L}$, respectively. The EBCCT was 4 min, and flow rate was 204 mL/min. Q_{10} represents the As adsorption capacity when the effluent As concentration $<10 \mu\text{g/L}$.

could facilitate the immobilization of adsorbed As, because As(V) surface complexes on metal oxides are reported to be more stable than As(III).²⁷ However, the total As adsorption capacity might be lowered upon As(III) oxidation since the As(III) adsorption capacity was higher than that of As(V) at pH 8.2 (Figure 1).

Adsorption of Coexisting Ions. To study the impact of coexisting ions in groundwater on As removal during filtration, concentrations of major anions and cations before and after the TiO_2 filters were compared (Figures S4 and S5). Among the common coexisting ion candidates, Mn^{2+} , Fe^{3+} , F^- , and PO_4^{3-} were below their detection limits in the raw groundwater (Table S1), thus they were not the focus of this study. Meanwhile, concentrations of Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , Cl^- , Br^- , and NO_2^- remained the same in the influent and effluent (Figures S4 and S5), and therefore their effects on As removal were also negligible. Among all ions, only Si(OH)_4 , Ca^{2+} , and HCO_3^- (Figure 2-II, -III, and -IV, respectively) were appreciably adsorbed on TiO_2 , and therefore their effects on As removal in TiO_2 filters merited mechanistic study at the molecular level.

Si(OH)₄ Effect on As Removal. The high Si(OH)_4 adsorption capacities (10.3–14.3 mg/g, 0.367–0.509 mmol/g, as shown in Figure 2-II) might greatly interfere with As adsorption since Si(OH)_4 is a structural analog to As(V). The inhibition effect is widely reported and ascribed generally to competitive adsorption.²⁸ To investigate the effect of Si(OH)_4 adsorption on the As(V) surface structure on a molecular scale, As *K*-edge EXAFS analysis for samples with coexisting Si(OH)_4 and As(V) were conducted, and the results are shown in Figure 4 and Table S5. The strong FT signal at 1.70 Å was resolved to contributions from four As–O bonds in the first shell for all samples.

In the As(V)– TiO_2 adsorption sample, the second FT peak was attributed to the As–Ti bonding at 3.27 Å with 1.8 Ti atoms (Figure 4 and Table S5). The As–Ti distance and coordination number (CN) indicated the formation of the As(V) bidentate binuclear complex on the TiO_2 surface.²⁹

In the Si(OH)_4 and As(V) coexisting samples, only an As–Ti single scattering (SS) path was resolved in the second shell. The As–Ti atomic distances (3.27–3.28 Å) and CN (1.3–1.7)

Figure 4. Observed (points) and simulated (lines) k^3 -weighted As *k*-edge EXAFS spectra (I) and their corresponding Fourier transform magnitudes (II) and real parts (III) of 5.0 mM As(V) and As(V) in the presence of Si(OH)_4 adsorption on TiO_2 at pH 8.2 in 0.04 M NaClO_4 solution, and the molar ratio of Si/As was 50 and 100, respectively.

were similar to those in the As(V)– TiO_2 adsorption sample, implying that the presence of Si(OH)_4 (Si/As = 50–100, molar ratio) would not impact on As(V) structural configurations on TiO_2 . Therefore, the competitive adsorption of the structural analog Si(OH)_4 would not change the surface As(V) configuration but would occupy the available surface sites.

Besides competing for the surface sites, the polymerization of Si(OH)_4 on metal oxides may block the surface sites and consequently inhibit As(V) adsorption.^{30–32} The amount of Si(OH)_4 surface oligomer and polymer may increase with time and, even worse, may not be desorbed by As(V).³² As shown in our following TiO_2 regeneration results, low Si(OH)_4 desorption, due to Si(OH)_4 polymerization, may contribute to the decreased As adsorption capacity in the regenerated TiO_2 column.

Thus, the presence of Si(OH)_4 in groundwater may be one of the most important reasons for the exhaustion of As absorption capacity. To use and regenerate the As adsorbents efficiently, the groundwater filtration should be completed in a short period of time before Si oligomer and polymer species colonize TiO_2 surface sites.

Ca^{2+} Effect on As Removal. To study the interference of Ca^{2+} toward As(V) molecular structures, the As *K*-edge EXAFS of coexisting Ca^{2+} and As(V) samples and the groundwater adsorption sample were performed and the results are shown in Figure 5 and Table S6.

In the Ca–As(V)– TiO_2 ternary samples, mixed As–Ti and As–Ca SS paths were considered to fit the second shell, and the model resolved 1.4–1.8 Ti atoms at the distance of 3.27–3.28 Å and 0.6–1.4 Ca atoms at 3.56–3.61 Å. The CN of the As–Ca path was less than unity in some of the samples, which may be attributable to a monodentate mononuclear As complex with H-bonding to an adjacent singly coordinated OH group.³³ Furthermore, the significance of adding an additional As–Ca path in ternary samples was justified using the *F*-test.³⁴ The *F*-test results show that the confidence level with the inclusion of the As–Ca SS path was 88.6–95.3% (Table S7), significantly higher than the required value of 67%,³⁴ confirming the appropriateness of addition of this As–Ca to the As–Ti path. In addition, the As–Ca atomic distance (3.56–3.61 Å) in the As and Ca^{2+} coadsorption samples was close to that in As(V)–Ca precipitates (3.56 Å). Thus, the EXAFS analysis implies that

Figure 5. Observed (points) and simulated (lines) k^3 -weighted As k -edge EXAFS spectra (I) and their corresponding Fourier transform magnitudes (II) and real parts (III) of 5.0 mM As(V) (a) and As(V) in the presence of Ca^{2+} adsorption on TiO_2 at pH 8.2 in 0.04 M NaClO_4 solution. The groundwater sample was collected in the 10 g TiO_2 column, and the sample precipitate was prepared by reacting 7.5 mM CaCl_2 with 5.0 mM As(V) solution at pH 8.2.

the As–Ca and As–Ti bonds coexist, suggesting the formation of a Ca–As(V)– TiO_2 ternary complex.

In the groundwater adsorption sample, As–Ti bonding at 3.27 Å with 1.6 Ti atoms and As–Ca bonding at 3.59 Å with 0.7 Ca atoms were observed (Table S6). The As–Ti and As–Ca distances are in accordance with the previous values of 3.30 Å for As–Ti²¹ and 3.46–3.63 Å for As–Ca.³⁵ The significance of adding this additional As–Ca scattering also passed the F -test (98.5%, Table S7), suggesting that the Ca–As(V)– TiO_2 ternary surface complex was formed. In accord with our present study, such a ternary surface complex is attributable to the elevated coadsorption of Ca^{2+} in the presence of phosphate, the structure analog of As(V).³⁶

The formation of the Ca–As(V)– TiO_2 ternary complex would subsequently increase As(V) and Ca^{2+} adsorption capacities.³⁷ Our PHREEQC modeling results show that the breakthrough of As(V) would be substantially sooner without considering this Ca–As(V)– TiO_2 ternary complex (Figure S6-I). Ca^{2+} and Mg^{2+} have been assumed to have similar adsorption behaviors on iron oxides in previous studies.^{9,38} However, the adsorption capacity of Ca^{2+} (63.0 mg/g, 1.575 mmol/g) was much larger than Mg^{2+} (2.97 mg/g, 0.124 mmol/g) in the present study (Figure 2), demonstrating that the formation of the Ca–As(V)– TiO_2 surface complex could greatly enhance Ca^{2+} adsorption.

HCO_3^- Effect on As Removal. Similar to $\text{Si}(\text{OH})_4$ and Ca^{2+} , a considerable amount of HCO_3^- (31.8 mg CaCO_3/g TiO_2) was adsorbed on TiO_2 (Figure 2-IV). Therefore, HCO_3^- adsorption was included in the model, resulting in a satisfactory simulation of breakthrough curves for As and HCO_3^- . The effect of HCO_3^- on As removal was further evidenced by the overestimation of the As filtration cycle by PHREEQC without considering it (Figure S6-II). In addition, the breakthrough curves for As, $\text{Si}(\text{OH})_4$, Ca^{2+} , and HCO_3^- were all well simulated with the inclusion of HCO_3^- adsorption (Figure 2); the curves could not be fitted well otherwise without the inclusion of HCO_3^- adsorption (Figure S7).

Compared with other competing ions, HCO_3^- is reported to have a less adverse effect on As adsorption than Si and phosphate.¹⁰ However, the coexistence of $\text{Ca}^{2+}/\text{Mg}^{2+}$ with HCO_3^- in groundwater could facilitate the release of adsorbed As due to the competitive formation of aqueous As–Ca– HCO_3^-

complexes.¹¹ This synergistic effect may partly contribute to the release of As from the TiO_2 column in the early breakthrough stage.

Compound Effects of $\text{Si}(\text{OH})_4$, Ca^{2+} , and HCO_3^- . The breakthrough curves of As, Ca^{2+} , $\text{Si}(\text{OH})_4$, and HCO_3^- in the small 10-g TiO_2 filters were well simulated with the PHREEQC model, which integrates batch adsorption reactions with one-dimensional reactive transport (Figure 2 and Table S3). The model simultaneously considered the adsorption of As, Ca^{2+} , $\text{Si}(\text{OH})_4$, and HCO_3^- , and the formation of Ca–As– TiO_2 ternary surface complexes as determined by our spectroscopic analysis (Tables S6–S7). Without the inclusion of coexisting ions, the model-predicted effluent As concentrations would increase rapidly at about BV 1,500 (Figure S6-I).

To study the kinetic effects on As adsorption, the nonlinear equilibrium-kinetic transport module was included in the column modeling based on our previous kinetics study.⁶ Results showed that the inclusion of rate and kinetic modules has little effect in modeling the As breakthrough curves, and the modeling results were almost coincident with modelings only considering the compound effects of coexisting ions (Figure 2). Therefore, in our present study, the influence of coexisting ions on As adsorption was the major challenge in predicting groundwater As adsorption capacities in columns using batch parameters. Herein, by identifying and considering the effects of interfering ions, the As breakthrough curves in the large 750-g TiO_2 field column could be successfully predicted (Figure 3) with adsorption constants obtained from batch experiments and transport parameters determined from the small column. Our present study may shed new light on the integration of molecular-level mechanistic study with macroscopic field groundwater filtration.

Phosphate can greatly inhibit As adsorption due to its structural similarity to oxyanions of As.³⁹ Moreover, phosphate can replace the adsorbed arsenic as demonstrated in previous studies.^{10,40,41} Therefore, the effect of phosphate on As adsorption should be carefully considered in the prediction of groundwater filtration when phosphate is present.

TiO_2 Regeneration. The spent TiO_2 could be regenerated with successive 2 mol/L NaOH and HCl treatments using a solid/liquid ratio of 1:10. The As desorption rate could reach 99.5% for the first regeneration and 98.7% for the second one. The desorption rates were 86.8–88.6% for Ca^{2+} and 45.9–48.2% for $\text{Si}(\text{OH})_4$ (Figure S8). The low $\text{Si}(\text{OH})_4$ desorption rate could be ascribed to the polymerization of $\text{Si}(\text{OH})_4$ on the TiO_2 surface during the long-term filtration cycle.⁴² Compared with iron oxides, the TiO_2 absorbent was stable in the alkali wash and acid pickling, and no dissolved Ti^{4+} was detected in the NaOH and HCl solutions or in the treated groundwater.

To recover the As from the spent NaOH solution and avoid secondary pollution, the NaOH regeneration solution was heated at 70 °C for 10 h. After evaporation, about 10.17 g of solids remained, where 78.7% (8 g) was NaOH, 6.2% (0.63 g) was Si, 1.4% (0.14 g) was adsorbed Ca, and 0.2% (0.25 g) was As by mass balance calculation. Our XRD analysis indicates that the major constituents were NaOH and As_2O_5 (Figure S9), corresponding to a sodium arsenate mixture.

Impacts to Human Health. The first morning void urine samples of four volunteers from the local residence where the column was installed were collected before and after they ingested the treated groundwater (Figure 6). The total As concentrations, ranging from 972 to 2,080 $\mu\text{g}/\text{L}$ before groundwater treatment, decreased to the range 31.7–73.3

Figure 6. Urinary As concentrations of four volunteers before and after drinking treated groundwater in the study site (points) and the pseudo-first-order kinetics model (lines).

$\mu\text{g/L}$ at the end of the experimental cycle (15–33 days). Notably, $1,490 \pm 92 \mu\text{g/L}$ urinary As was detected for the volunteer who drank the As-tainted groundwater for only 2 weeks (Figure 6-II).

Before the ingestion of As-free groundwater, DMA was the major As species in urine with a mean concentration of 475–1,300 $\mu\text{g/L}$, followed by As(III) (206–600 $\mu\text{g/L}$), MMA (123–439 $\mu\text{g/L}$), and As(V) (42.4–131 $\mu\text{g/L}$) (Figure 6). The proportion of As species was in agreement with a previous study and showed that methylated As species metabolized in the liver are preferentially excreted through urine.⁴³ The variability of methyl arsenic concentrations between the four volunteers could be due in part to the genetic variability in the arsenic methyltransferase (AS3MT) gene in different individuals.⁴⁴ Analysis of more urine samples should improve the understanding of variability between humans in the efficiency of As metabolism.⁴⁵ After the groundwater was treated, the percentages of the four As species in urine remained the same, suggesting the As metabolic pathway was not changed after As removal from groundwater.

The background urinary As levels are 10 $\mu\text{g/L}$ in European countries and in the United States,⁴⁶ and 9.1 $\mu\text{g/L}$ in the control adult group in Inner Mongolia, China.⁴⁷ The urinary As concentrations in our present study at the end of the experimental cycle still exceeded the background levels after people drank the As-free groundwater. The decrease in urinary total As followed pseudo-first-order kinetics (Figure S10), and this kinetics model has been successfully used to describe drug metabolism in the human body.⁴⁸ However, our model overestimated the excretion process and predicted that after 20 days the urine As may be lower than 10 $\mu\text{g/L}$. The difference between model prediction and observation highlights that the As excretion from the body is a complicated long-term process, and other As ingestion pathways such as As-containing foods should be avoided. Although this is not a complete study of retention of As in people switching to low-As drinking water, it provides new information on how long it takes for urinary As to decrease upon As removal.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01520.

Details of groundwater parameters; As speciation analysis; EXAFS; CD-MUSIC; PHREEQC modeling; TiO_2 regeneration; and additional figures and tables (PDF)

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Notes

The authors declare no competing financial interest.

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