

Surface Complexation of Ferrous Iron and Carbonate on Ferrihydrite and the Mobilization of Arsenic

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Surface complexation models are commonly used to predict the mobility of trace metals in aquifers. For arsenic in groundwater, surface complexation models cannot be used because the database is incomplete. Both carbonate and ferrous iron are often present at a high concentration in groundwater and will influence the sorption of arsenic, but the surface complexation constants are absent in the database of Dzombak and Morel. This paper presents the surface complexation constants for carbonate and ferrous iron on ferrihydrite as derived for the double-layer model. For ferrous iron the constants were obtained from published data supplemented by new experiments to determine the sorption on the strong sites of ferrihydrite. For carbonate the constants were derived from experiments by Zachara et al., who employed relatively low concentrations of carbonate. The double-layer model, optimized for low concentrations, was tested against sorption experiments of carbonate on goethite at higher concentration by Villalobos and Leckie, and reasonable agreement was found. Sorption was also estimated using linear free energy relations (LFER), and results compared well with our derived constants. Model calculations confirm that sorption of particularly carbonate at common soil and groundwater concentrations reduces the sorption capacity of arsenic on ferrihydrite significantly. The displacing effect of carbonate on sorbed arsenate and arsenite has been overlooked in many studies. It may be an important cause for the high concentrations of arsenic in groundwater in Bangladesh. Sediments containing high amounts of sorbed arsenic are deposited in surface water with low carbonate concentrations. Subsequently the sediments become exposed to groundwater with a high dissolved carbonate content, and arsenic is mobilized by displacement from the sediment surface.

Introduction

The widespread, high As concentration in Bangladesh groundwaters threatens the lives of millions of people.

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Currently, three theories have been advanced to explain the high As concentrations in Bangladesh groundwater as the result of hydrogeochemical reactions. One theory relates the high As concentration to reduction and dissolution of iron oxyhydroxides to which As was naturally bound during the deposition of sediment in the delta (1, 2). Another theory considers reduction of sorbed As in the aquifer and desorption of less strongly bound arsenite as the major factor (3). The third theory invokes the oxidation of arsenic-containing pyrite, formed in the sediments during an earlier reductive step in which sulfate was reduced and arsenic was scavenged.

However, all of these theories do have some inconsistencies. The pyrite oxidation theory calls upon an extensive groundwater drawdown to enable the increased passage of oxygen via gaseous diffusion to pyritic sediment. However, a general drawdown is unlikely in the regularly flooded lowlands of Bangladesh. Nickson et al. (1) noted contradictions in their iron reduction theory, namely, a lack of correlation of Fe and As concentrations in groundwater and an $\text{Fe}^{2+}/\text{HCO}_3^-$ ratio that is much too small. Also, if iron oxyhydroxide is the sole electron acceptor for oxidation of organic matter, the pH would become much higher than observed, even if siderite (FeCO_3) would precipitate. The other reduction theory comprises desorption of arsenite but does not explain why in many groundwater samples with a high As concentration, arsenate is still the major species (special study areas of the British Geological Survey, 4).

Displacement of arsenic by dissolved carbonate is in this paper proposed as an alternative mechanism for the genesis of high arsenic groundwater. To calculate the speciation of trace metals among oxides in contact with river water, soil water, and groundwater (5–11) and in water treatment (11, 12), surface speciation models are commonly employed. The standard choice incorporated in geochemical models (13, 14) is Dzombak and Morel's (D&M) database (15) for metal and anion sorption on ferrihydrite (hydrated ferric oxide, Hfo). Unfortunately, the database does not comprise constants for Fe^{2+} and HCO_3^- . These species often have a high concentration in Bangladesh groundwater and may influence the sorption of arsenic on the sediment.

Sorption of carbonate is well-known to be strong (16) and to shift the point of zero charge (PZC), the zeta potential, and the proton buffering capacity of oxides (17–22). It also affects the sorption of chromate (23, 24) and forms ternary surface complexes with U and Pb (25–27). Surprisingly, carbonate was found to enhance sorption of sulfate and selenate anions at small concentrations (28). Zachara et al. (23) have measured carbonate adsorption on ferrihydrite and modeled the data with the triple-layer model (29). The total carbon concentration in their experiments was $4.6 \mu\text{M}$, which is much smaller than is found in natural waters and, consequently, constants derived from these laboratory data may not be applicable in a model for the natural environment. Van Geen et al. (24) and Villalobos and Leckie (30, 31) have recently published data on CO_2 sorption on goethite that span a larger concentration range. They modeled the data with the triple-layer model (29) and the double-layer model (15, 32).

Sorption constants for Fe^{2+} on ferrihydrite can be estimated to lie in the range of those for Cd^{2+} and Zn^{2+} (11). The concentration of Fe^{2+} in anaerobic groundwater may be 1000 times (or more) higher than of these heavy metals, and Fe^{2+} will then dominate the majority of the strong sorption sites. Sorption edges of Fe^{2+} on various iron oxides have also been reported (33–35) and were fitted with the constant capacitance model by Liger et al. (35).

TABLE 1. Surface Complexation Constants for the Ferrihydrite Double-Layer Model Optimized in This Study^a

Carbonate		
Hfo_wOH + CO ₃ ²⁻ + H ⁺ =	Hfo_wOCO ₂ ⁻ + H ₂ O	log K = 12.78 ± 0.48
Hfo_wOH + CO ₃ ²⁻ + 2H ⁺ =	Hfo_wOCO ₂ H + H ₂ O	log K = 20.37 ± 0.20
Fe ²⁺		
Hfo_wOH + Fe ²⁺ =	Hfo_wOFe ⁺ + H ⁺	log K = -2.98 ± 0.30
Hfo_wOH + Fe ²⁺ + H ₂ O =	Hfo_wOFeOH + 2H ⁺	log K = -11.55 ± 0.23
Hfo_sOH + Fe ²⁺ =	Hfo_sOFe ⁺ + H ⁺	log K = -0.95 ± 0.5

^a Uncertainty interval indicates the approximate 95% confidence limits.

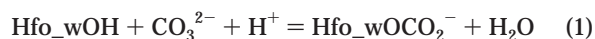
Here, the D&M compatible sorption constants for Fe²⁺ and CO₃²⁻ are determined to extend the applicability of the D&M database. The CO₂ sorption experiments with goethite (24, 30) are investigated as a means for validating the proposed extrapolations from the experiments of Zachara et al. Sorption envelopes, calculated with data-optimized and estimated constants, are compared. Example calculations illustrate the important effects of these species on the sorption of Cd, Pb, and As. The relationship between HCO₃⁻ and As concentrations in groundwater (1, 36, 37) is reinvestigated in light of the displacing action of (bi-)carbonate ions for sorbed As on iron oxyhydroxide. An increasing carbonate concentration can significantly enhance As desorption and probably does contribute markedly to observed high As concentrations in Bangladesh groundwater.

Computations

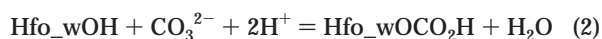
Model fits were optimized with the least squares, nonlinear parameter estimation program PEST (38) in combination with PHREEQC-2 (14) as illustrated in the Supporting Information. The basic data for the modeling were obtained from tables as published or by digitizing graphs.

Sorption of CO₃²⁻. Zachara et al. (23) measured carbonate adsorption in ferrihydrite suspensions spiked with ¹⁴C-labeled NaHCO₃ at a concentration of 4.6 μM total carbon, over a pH range of 5.5–9.0. For the model here, the properties of ferrihydrite were defined according to the values proposed by D&M (surface area = 600 m²/g, pK_{a1} = 7.29, pK_{a2} = 8.93, 0.87 mM Fe = 78 mg of ferrihydrite/L with 0.174 mM sites, for anions only the weak sites are active).

Two complexes were included in the optimization, the uncharged complex Hfo_wOCO₂H and the singly charged complex Hfo_wOCO₂⁻, which result from surface-OH ligand-exchange by bicarbonate and carbonate ions, respectively:



and



The combination of these complexes provided a better fit than provided by the uncharged complexes (SOH₂-HCO₃)⁰ and (SOH-H₂CO₃)⁰ (23), which are indiscernible in the double-layer model. The optimized constants are listed in Table 1, and the fit is shown in Figure 1. The confidence limits in Table 1 provide only an indication of parameter uncertainty, as they rely on a linearity assumption that may not extend as far in parameter space as the confidence limits themselves. Nevertheless, the smaller 95% confidence interval for the uncharged complex indicates that it is more important for explaining the data. The fit shown in Figure 1 is similar to the one obtained with the triple-layer model (23).

The applicability of the derived constants for higher concentrations of total carbon can be tested on experiments with goethite (24, 30). Sorption of carbonate species on different iron oxides (goethite and hematite) has been found

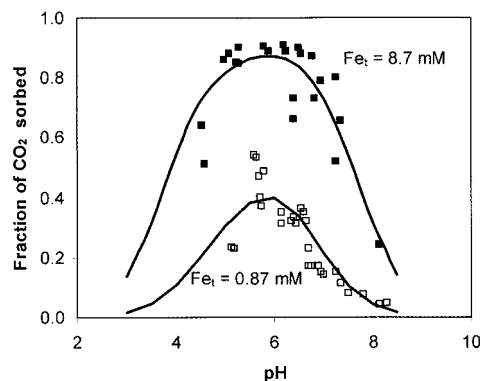


FIGURE 1. Sorption of CO₂ on ferrihydrite in 0.1 N NaNO₃. Data points are from Zachara et al. (23), lines are from optimized ferrihydrite double-layer model with standard sorption site density, and pK_a values are for ferrihydrite.

to be comparable on a *per site* basis (24), and also Manceau (39) proposes that sorption of oxyanions occurs on structurally similar sites on goethite and ferrihydrite. Van Geen et al. (24) measured CO₂ sorption on goethite as a function of pH in an ingenious reaction vessel with tubing for transferring small amounts of headspace gas to a gas chromatograph. Villalobos and Leckie (30) repeated the experiments of Van Geen et al., and their experimental data for 63 μM total carbonate are compared in Figure 2a with the ferrihydrite model predictions (constants from Table 1), both expressed as surface coverage in micromoles of carbonate per square meter. The ionic strength effect and the peak values are matched, but the calculated sorption envelopes are shifted by 1 pH unit. The pH shift could be related to the different PZC values of ferrihydrite (PZC = 8.11) and goethite (PZC = 9.1), and the constants were reoptimized, using pK_{a1} = 8.1 and pK_{a2} = 10.1. However, the description remained inadequate. The fit also did not improve when pK_a values were included as variables in the optimization, indicating that the speciation model for carbonate was incorrect.

The triple-layer model fit of the same data greatly improved when Hiemstra and Van Riemsdijk's (40) concept of charge distribution was applied (31), namely, when the charge of the carbonate complex was distributed over the oxygens at different distances from the surface instead of being condensed in a point charge. Sorption in the triple-layer model is conceived to occur in three layers or planes with different potentials. The 0 plane is located at the surface oxygens of the oxide, and protons and inner-sphere complexes bind there (32, 41). The β plane is where the ions from background electrolytes form outer-sphere complexes and where two oxygens of a monodentate bound ≡OCO₂⁻ group reside (31, 40, 42). Villalobos and Leckie (31) attributed almost all of the charge of the ≡OCO₂⁻ complex to the β plane instead of the 0 plane. The capacitances of the 0 and β planes were 1.1 and 0.2 F/m², respectively (with NaCl as electrolyte, 31), and the major effect of the charge distribution is that allocating the negative charge of ≡OCO₂⁻ to the β plane

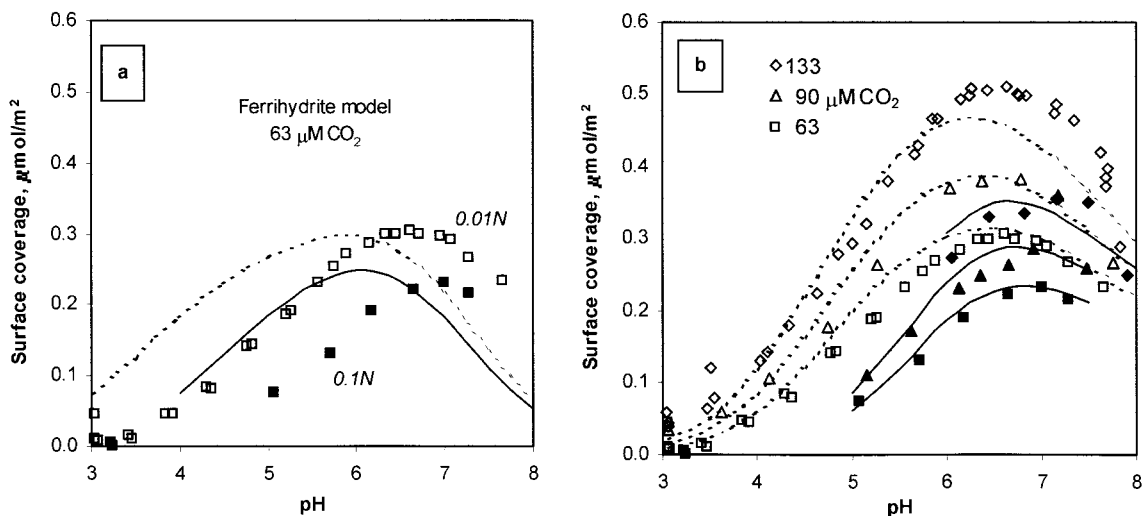
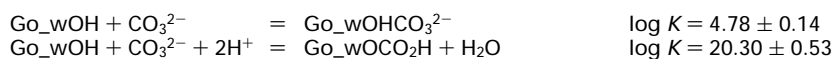


FIGURE 2. Sorption of CO₂ on 2 g of goethite/L in 0.01 N (open symbols, dotted lines) and 0.1 N (solid symbols, full lines) NaCl: (a) ferrihydrite model; (b) optimized goethite double-layer model with doubly charged carbonate complex. Data points are from Villalobos and Leckie (30).

TABLE 2. Surface Complexation Constants for Carbonate Sorption in the Goethite Double-Layer Model^a

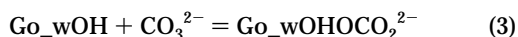
closed system, 2 g of goethite/L, 70 m²/g, pK_{a1} = 8.1, pK_{a2} = 10.1



^a Data from Villalobos and Leckie (30). Uncertainty interval indicates the approximate 95% confidence limits.

decreases the potential at the surface 5 times more than attribution of the charge to the 0 plane would do. The resulting lower potential will enhance proton adsorption, and the charge distribution model is helpful for fine-tuning the pH dependence of the sorption envelope.

In the double-layer model, a charge redistribution is not possible because all of the complexing species are placed at the surface. However, the effect of charge distribution in the electrostatic model can be simulated by increasing the negative charge on the sorbed carbonate complex, as this will also decrease the surface potential. Thus, in the goethite double-layer model a doubly charged complex was introduced:



Go_w represents the sorption site in the goethite double-layer model. This doubly charged complex provided a much better fit than the single-charge surface complex, as is shown in Figure 2b (constants in Table 2). The 95% confidence intervals indicate that the doubly charged complex is the most important. Apparently, the speciations of carbonate on goethite and ferrihydrite are different, a conclusion that was drawn also from the different infrared spectra (21). Nevertheless, the performance of the double-layer model in the open system measurements of Villalobos and Leckie (30) where total CO₂ concentrations increase to 6 mM may provide a clue to the validity of the model predictions for such high concentrations. Results for the highest CO₂ pressure are presented in Figure 3. The model overestimates sorption by a maximum of 0.3 log unit for pH < 5 but improves somewhat at higher pH. For pH > 8, and at atmospheric CO₂ pressure, the model was found to underestimate sorption. Villalobos and Leckie invoked sorption of the NaHCO₃ complex to explain the observed increase, but this complex has no significant contribution in the double-layer model. Apparently, the double-layer model is less well equipped for

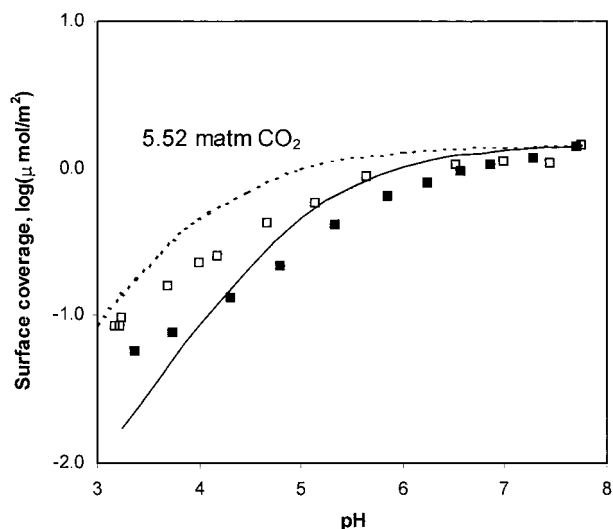


FIGURE 3. Sorption of CO₂ at P_{CO₂} = 5.52 matm on 14.7 g of goethite/L in 0.01 N (open symbols, dotted line) and 0.1 N (solid symbols, full line) NaCl. Data points are from Villalobos and Leckie (30), and lines are from goethite double-layer model optimized on closed system data (Figure 2b).

modeling CO₂ sorption over a large concentration range than the triple-layer model, and sorption at total carbonate concentrations of natural waters may be incorrect by a factor of ~2 (=10^{0.3}).

Sorption of Fe²⁺. Liger et al. (35) determined sorption of Fe²⁺ on ferrihydrite as a function of pH. They used 0.21 g of ferrihydrite/L with a surface area of 244 m²/g and a site density of 2.27/nm², which gives 0.193 mM sorption sites. The ferrihydrite had pK_{a1} = 7.70 and pK_{a2} = 9.05 (recalculated from conditional constants for I = 0.1 mol/L). The total concentration of Fe²⁺ was 0.16 mM in 0.1 M NaNO₃. The

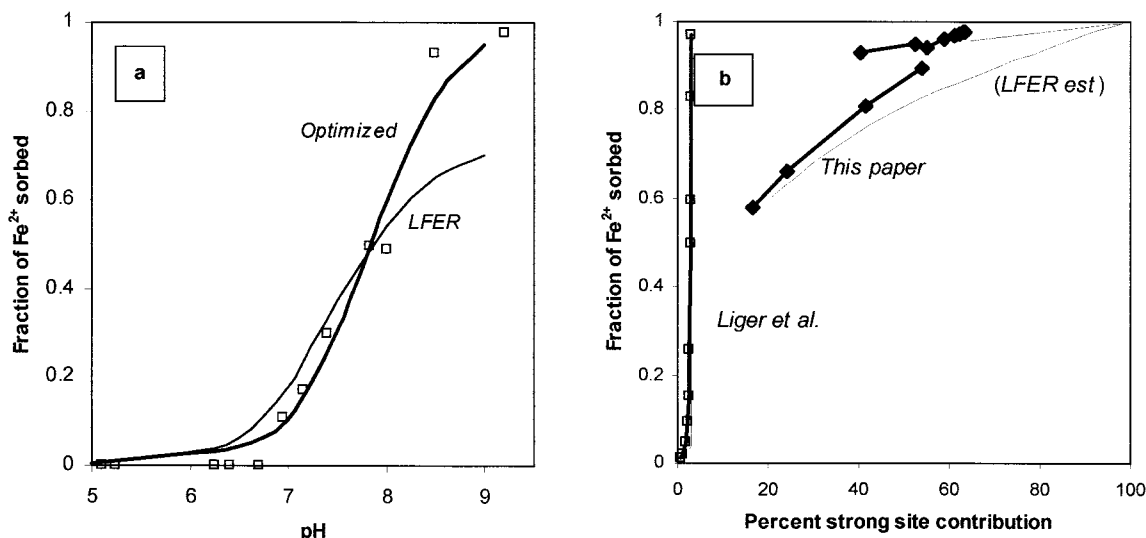


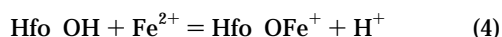
FIGURE 4. Sorption edge of 0.16 mM Fe²⁺ on ferrihydrite in 0.1 N NaNO₃, with experimental data from Liger et al. (35) (a) and contribution of strong sites on these and new experiments at pH 7.0 with increased concentration of ferrihydrite (b). The full, thick line is for the optimized model, and the thin line is for the model with surface complexation constants estimated with linear free energy relations.

TABLE 3. Results of Experiments at High Hfo/Fe²⁺ Ratio in 0.1 M NaNO₃^a

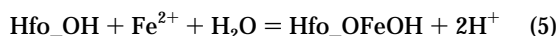
pH	mM FeOOH	mM Fe ²⁺	
		total	aqueous
7.10	86.7	0.0074	0.0000
7.10	86.6	0.0120	0.0000
7.08	85.8	0.0397	0.0003
7.05	84.9	0.0678	0.0015
7.01	83.3	0.1240	0.0042
6.94	80.7	0.2155	0.0128
7.01	78.0	0.3059	0.0162
7.01	68.3	0.5880	0.0495
7.19	14.6	0.0267	0.0029
7.08	14.6	0.0885	0.0165
6.97	14.5	0.2430	0.0814
6.92	14.4	0.3980	0.1680

^a Ferrous iron was added as ferro-sulfate salt. Column labeled "aqueous" gives solute Fe²⁺ after adsorption.

data were modeled (35) with the constant capacity model, with two complexes



and



for one type of site. The data were fitted to the D&M database with 0.188 mM weak sites and 4.71 μM strong sites, on 0.143 g of ferrihydrite with a surface area of 600 m²/g. The unidentate, monohydroxy neutral species was included for the weak sites only, in agreement with other species in ref 15. Initially, the association constant for the strong sites was fixed to log *K* = 0.7, estimated using LFER (discussed next). However, its value proved to be unimportant in modeling the experimental data of Liger because the contribution of the strong sites to the sorbed concentrations was relatively small. Additional experiments were done at pH 7.0 following the procedures of Liger, but with about 20 or 100 times higher concentration of ferrihydrite and lower concentrations of Fe²⁺ (Table 3). The data did allow for optimization of the surface complexation constant for the strong sites. The concentration of surface sites on the newly prepared ferri-

hydrite appeared to be different from that of Liger et al. and was included in the optimization, with the ratio of the weak and the strong sites fixed to give 97.5% weak and 2.5% strong sites. The optimized numbers of weak and strong sites for these experiments were 0.21 and 5.4 × 10⁻³ mol/mol of ferrihydrite, respectively. The data fit is shown by the thick lines in Figure 4, and the constants are noted in Table 1.

Discussion

Estimating Species and Constants with LFER. Dzombak and Morel (15) have suggested linear free energy relations (LFER) among surface complexation constants and aqueous hydroxy complexes. The values for Fe²⁺ can be estimated to be for weak and strong sites, respectively



and



by interpolation, using the data for Zn²⁺ and Cd²⁺. The neutral monohydroxy species of eq 5 is not considered by D&M for transition metals. Slightly different *K* values are obtained with the formulas derived for the complete dataset in ref 15. However, the hydrolysis constant for Fe²⁺ lies between those for Zn²⁺ and Cd²⁺, and the *K* values based on these ions do provide a quite good estimate for Fe²⁺ sorption when the pH is <8, as is shown in Figure 4a. For pH values >8, the estimated sorption edge levels off because the D&M model does not consider sorption of the hydroxy complex for transition metal ions. Nevertheless, the remarkably good estimate, obtained by LFER with species that are not redox-sensitive, indicates that the sorption edge of Fe²⁺ shown in Figure 4a is due to sorption only and is not influenced by oxidation (34). This was further confirmed by desorbing Fe²⁺ at pH 3.0 in the experiments with 14.5 mM ferrihydrite (Table 3).

The strong sites have only a small contribution to the sorption edge in the experiments of Liger et al., and the log *K* for the strong sites was found to be immaterial, as is shown in Figure 4b where the thin line from the LFER estimate coincides with the thick line from the optimized model. In our experiments, the contribution of the strong sites varies from 17 to 63% of the fraction of Fe²⁺ sorbed. From these data, the surface complexation constant for the strong sites

TABLE 4. Effect of Including Carbonate and/or Ferrous Iron Sorption on Dimensionless Distribution Coefficients (K_d) for Heavy Metals among Ferrihydrite and Water

surface coverage (%)				$K_d(-)$			
carbonate	Fe ²⁺			As(III)	As(V)	Cd	Pb
0	0 (no complexes)			22	422	1.0	427
79	0 (carbonate complex)			5	23	0.7	303
0	9 (Fe ²⁺ complex)			20	446	0.8	314
78	3 (carbonate + Fe ²⁺ complexes)			5	27	0.5	246
61	0 (carbonate complex, low K) ^a			8	86	0.8	372

				Water Composition				
pH	pe	Ca ²⁺	Fe ²⁺	HCO ₃ ⁻	As(III)	As(V)	Cd ²⁺	Pb ²⁺
7.0	-0.21	100	5	315	5 × 10 ⁻³	5 × 10 ⁻³	10 ⁻³	10 ⁻³ mg/L

Ferrihydrite
89 mg/L, weak sites 0.2 mM, strong sites 0.005 mM, surface area 600 m²/g

^a log K for carbonate complexes at low end of 95% confidence limit.

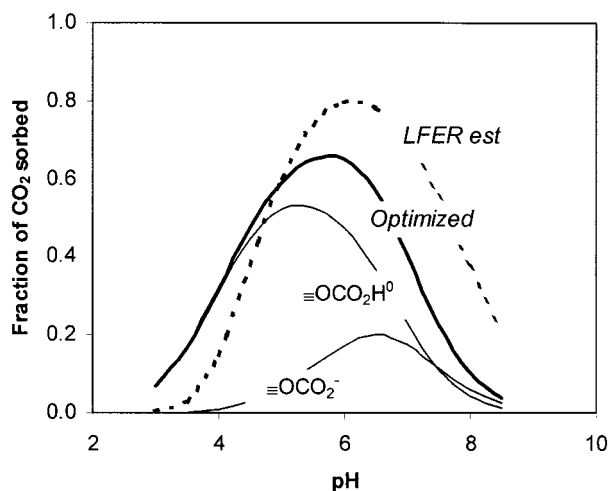


FIGURE 5. Sorption of carbonate species on 0.15 g of ferrihydrite/L in 0.1 N NaNO₃ (cf. Figure 1). Full lines are for the ferrihydrite double-layer model, and the dotted line is for the Hfo_wOCO₂⁻ species with a complexation constant estimated using LFER.

was optimized to log $K = -0.95$, which is much smaller than the LFER estimate.

For anions, D&M suggest a LFER of the surface complexation constant with the second dissociation constant of the acid anion. The estimated constant for the carbonate complex Hfo_wOCO₂⁻ (reaction 1) is log $K = 13.86$. The optimized value is log $K = 12.78$. However, in the optimization, it was necessary to use also an uncharged complex (reaction 2), which D&M reserve for trivalent anions only. The uncharged complex is needed for modeling carbonate sorption at pH < 4.5, and it is the dominant complex in the optimized model (Figure 5). With only the single-charge complex, sorbed concentrations are too small at low pH and, conversely, too high at pH 6, where sorption is maximal. However, the overall trend of the sorbed fraction is well followed with the LFER estimated complex (Figure 5).

The binding strengths of the neutral complex are nearly the same for goethite and ferrihydrite in the double-layer model (cf. Tables 1 and 2), and given the nearly identical intrinsic K values for chromate and phosphate in the double-layer models for ferrihydrite and goethite (43), one could hope that the double-layer model would have the same intrinsic constants for oxyanions sorbed to any iron oxyhydroxide. However, the doubly charged complex invoked for goethite did not improve the double-layer model for ferrihydrite. The doubly charged complex has the form of an

outer-sphere complex (without ligand exchange with the surface hydroxyl), whereas, generally, the oxyanion complexes on goethite are considered to be inner-sphere for carbonate (21, 31) and for As (42, 44, 45). Contrary to the physical interpretation of charge distribution for carbonate complexation in the triple-layer model, the doubly charged complex in the double-layer model is an artifact that is nevertheless effective for shifting the carbonate sorption maximum to the observed pH because the surface potential is decreased and the proton is removed from the reaction equation (compare reactions 1 and 3).

Effects of Sorption of CO₃²⁻ and Fe²⁺ on Oxyanion and Heavy Metal Adsorption. Van Geen et al. (24) and Villalobos and Leckie (30, 31) concluded that carbonate species will cover a large part of the sorption sites of goethite at the CO₂ pressures which are encountered in soil water and groundwater. Anions are supposed to sorb only to the weak sites of ferrihydrite in the D&M database, and carbonate is thus especially important for limiting sorption of oxyanions such as selenate (28) and arsenite and arsenate; the effects of ternary complexes of carbonate and metals (25, 26) are here neglected. The importance of Fe²⁺ for modeling sorption of trace metals in anaerobic groundwater is due to the relatively high concentration of Fe²⁺ that will flood the strong sites and thus limit the sorption capacity for other metals. Moreover, sorbed Fe²⁺ catalyzes reduction reactions (34, 46), and it strongly reduces the desorption of other sorbed metals (34), but this may be caused by oxidation and occlusion in the precipitate.

An example calculation for a Ca-HCO₃ water type with 5 mg of Fe²⁺/L and heavy metals at trace concentrations will clarify the effects (Table 4). The sorbed concentrations on 1 mmol of ferrihydrite/L (equivalent to 0.2 and 5 × 10⁻³ mM weak and strong sites, respectively) were calculated in equilibrium with the groundwater composition given in Table 4, with and without Fe²⁺ and/or carbonate sorption. The dimensionless distribution coefficient K_d (ratio of sorbed and solute concentrations in moles per liter) shows dramatic variation. Including sorption of carbonate reduces the sorption of As(V) almost 20-fold and also reduces the sorption of Cd²⁺ and Pb²⁺ by about one-third because 70% of the weak sites are occupied by carbonate at a groundwater concentration of 315 mg of HCO₃⁻/L. Including sorption of Fe²⁺ also reduces the sorption of Cd²⁺ and Pb²⁺ by about one-third. It enhances the sorption of arsenate anions because the surface potential increases. When both Fe(II) and carbonate surface complexes are included, little arsenic and little cadmium may sorb on ferrihydrite. Finally, bringing the constants for carbonate to the lower limit of the estimated

TABLE 5. Model Concentrations of As in Groundwater in Bangladesh, with and without Carbonate Surface Complexes on Ferrihydrite

			Alk, mg of HCO ₃ ⁻ /L		mg of Fe ²⁺ /L	μg of As/L	
			without complex	with complex			
A = river water			260	0	1	1	
B ^a = (A) + CO ₂ (g) + calcite + 0.32 mM HFO			471	0	3	150	
C ^a = (B) + 0.282 mM C(0)			474	3	35	187	

A = River Water Composition									
pH	pe	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	As
8.39	12.24	19.3	4	14.1	55.7	9.6	260	4.4	10 ⁻³ mg/L

^a B and C are groundwater compositions with reactions (explained in text) imposed on infiltrating river water (A).

95% confidence interval reduces surface coverage by carbonate to 61%. Especially the sorption of arsenate increases again, because surface complexes of arsenate are negatively charged and thus more affected by a negative surface than arsenite, which is sorbed as a neutral species.

The notable effect of HCO₃⁻ that is concluded here may appear to disagree with experiments of Fuller et al. (47) and Meng et al. (48), who found a minor effect of HCO₃⁻ on coprecipitation of As in iron oxyhydroxide. However, the concentration of HCO₃⁻ in the experiments of Meng et al. (48) was obtained from laboratory air and was <0.01 mmol/L, which is 500 times smaller than in the example of Table 3. Fuller et al. (47) started with artificial streamwater with 3 mM total inorganic carbon (TIC) but purged it with air at pH 8.0, which should lower the TIC to <0.6 mM. Again, this is an order of magnitude less than is commonly found in groundwater. The small effects on As sorption noted by Wilkie and Hering (49) when adding 1 mM NaHCO₃ can be predicted well by the model, except for arsenite at pH 6, when desorption is predicted but no effect was observed. Also in this case, it is uncertain whether the actual CO₂ species distribution and concentrations had changed during the pH adjustment in the experiment.

Implications for As Concentrations in Bangladesh and West Bengal Groundwaters. High arsenic concentrations in groundwater are commonly correlated with high HCO₃⁻ concentrations (1, 36, 37). The increased HCO₃⁻ concentrations are usually associated with reducing conditions, under which arsenic takes the form of arsenite, which is less strongly sorbed than arsenate at pH 7 and for concentrations <1 μM As (49). Also, iron oxyhydroxide may be reduced and dissolved, which diminishes the sorption capacity of the aquifer (1, 37). However, recent experiments by Kim et al. (50) have shown that HCO₃⁻ by itself is effective in increasing the As concentration in dissolution experiments with pyrite containing rock, under both aerobic and anaerobic conditions. Kim et al. suggested that aqueous As-HCO₃ complexes form, which solubilize As. The displacing effect of HCO₃⁻ for As sorbed to iron oxyhydroxides, which is implied in the present paper, has not been considered so far.

The displacing effect of HCO₃⁻ may offer an explanation for high As concentrations in Bangladesh groundwater, given that the pH values and alkalinities of river water and groundwater are much different. The river water has a low CO₂ pressure of 10^{-3.0} atm and a high pH. The groundwater has a very high alkalinity of 474 mg of HCO₃⁻/L (average of the groundwater analyses, 4), which is related to the high CO₂ pressure of 10^{-1.09} atm on average, which develops in the soil at the high temperatures of the area. We can calculate the contribution of the various processes by first equilibrating river water with ferrihydrite. Subsequently, we imagine that river water infiltrates in a levee and gains a high CO₂ pressure of 10^{-1.09} atm while equilibrating with calcite and also with the river water-equilibrated ferrihydrite. In a third step, the

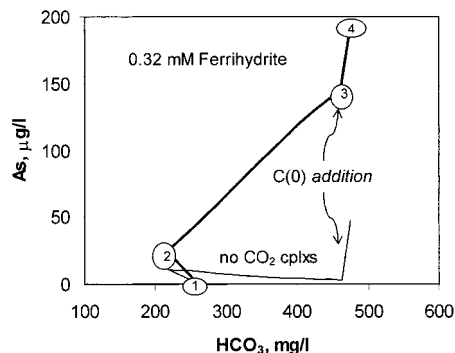


FIGURE 6. Modeled As concentration in Bangladesh groundwater as a function of the HCO₃ concentration with and without surface complexation of carbonate. The numbers on the curve are for (1) river water, (2) river water equilibrated with calcite, (3) after the CO₂ pressure had been increased, and (4) after C(0) had been added, which reduces ferrihydrite and releases As by decreasing the complexation capacity.

water encounters organic carbon, which reduces dissolved oxygen and ferrihydrite to give a concentration of 3 mg of Fe²⁺/L, the average concentration in the groundwater. The reduction of ferrihydrite will liberate the complexed ions in proportion. The river water composition from the BGS database (4) was used with 1 μg of As/L and equilibrated initially with 0.32 mmol of ferrihydrite/L. The concentration of ferrihydrite was selected to yield the observed average As concentration in the study areas of the BGS. The D&M surface complexation constants were used for As(III) and As(V), and the surface complexation capacity was coupled to the amount of ferrihydrite in PHREEQC-2 (14).

The calculations indicate that for the imposed conditions, bicarbonate displaces 147 ppb of As (cf. Table 5). In the river bank, where groundwater is still aerobic, the As concentration is calculated to be 150 ppb, compared with only 3 ppb for the case without carbonate surface complexes (composition B). Decrease of the complexation capacity due to reduction and dissolution of ferrihydrite adds another 37 ppb of As, to give 187 ppb of As (composition C). The latter is close to the average observed As concentration in groundwater (188 ppb in ref 4). Thus, the high alkalinity, which is primarily a result of a high CO₂ pressure in the soil zone, acts as the major driving force for high As concentrations in these groundwaters, and reduction of arsenic and iron oxyhydroxides and concomitantly of the sorption capacity is not even necessary as was believed until now (1-3).

The effect of increasing HCO₃⁻ on the As concentration in Bangladesh groundwaters is graphed in Figure 6. Again, 0.3 mM ferrihydrite was equilibrated with the river water containing 1 μg of As/L. CO₂ was added stepwise while equilibrium was maintained with calcite and ferrihydrite. In

the first step, As is released because the pH decreases due to precipitation of calcite (the river water is supersaturated with respect to calcite); this decrease of pH augments sorption of carbonate, which in turn imparts the surface with a negative charge and repels the arsenate anions. In the second step, CO₂ is added, calcite dissolves, and Figure 6 shows the gradual increase of the As concentration when alkalinity increases and As is displaced from ferrihydrite. In the third step C(0) was added to reduce ferrihydrite to give the average Fe²⁺ concentration of 3 mg/L in groundwater, and the As concentration leaps because sorption capacity is lost. On the other hand, the neglect of carbonate complexation decreases the As concentration in water with alkalinity, because sorption of As(V) is enhanced as pH decreases. The small initial increase of the As concentration in step 1 is now related to the redistribution of surface complexes of Mg²⁺ and H⁺, which, even though the pH decreases, lowers the surface potential at the ferrihydrite surface. In this case, the As concentration in groundwater increases only when ferrihydrite is reduced in the last step.

It should be noted that carbonate is not the only uniquely determining factor for high As concentrations in Bangladesh groundwater. The first and most important cause is that much arsenic is transported into the area as evidenced by the high As concentrations in river water. The BGS database gives a value of 29 ppb of As, and Kinniburgh (54) has found concentrations of 2–10 ppb at other locations and times in the area. Accordingly, the amount of As sorbed to ferrihydrite in the river sediments is high, and much As is available in the aquifers built from these sediments. Phosphate is undoubtedly active in displacing arsenic from the iron oxyhydroxides (51, 52). Including a phosphate concentration of 0.1 mg of PO₄³⁻/L in river water and increasing it to only 0.13 mg/L in groundwater has the same effect on model results as increasing the CO₂ pressure. Silicate and sulfate may also act as desorbers of As from ferrihydrite (49, 53), but the silicate concentrations are nearly equal in surface waters and groundwaters in the area, and the sulfate concentrations are quite variable. However, the silicate in river water (and also phosphate) may limit the amount of As that is sorbed on riverine iron oxyhydroxide. Furthermore, the concentration of 0.32 mM ferrihydrite was adopted in the calculations to yield approximately the observed arsenic concentration in groundwater. In the sediments, the iron and arsenic concentrations are much higher (1, 54), meaning that only a part of the arsenic is reacting while the major part is fixed, probably in the structure of the iron oxides (1, 47).

Despite these cautions, and although experiments with ferrihydrite and higher total carbonate concentrations are desirable to ascertain the effects of wider concentration variations, an important conclusion is that carbonate complexation must be incorporated in Dzombak and Morel's double-layer model when it is applied to simulate the behavior of trace metals in natural waters. The same conclusion holds for ferrous iron.

Acknowledgments

We thank Dr. Small for fine-tuning this paper for *ES&T* and David Kinniburgh and four reviewers for their comments. Dieke Postma provided valuable suggestions for the final manuscript. L.C. acknowledges partial financial support by IFCPAR.

Supporting Information Available

PHREEQC-2 input file for modeling Van Geen et al.'s (24) experiments on carbonate sorption on goethite. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Nickson, R. T.; McArthur, J. M.; Ravenscroft, P.; Burgess, W. G.; Ahmed, K. M. *Appl. Geochem.* **2000**, *15*, 403–413.
- McArthur, J. M.; Ravenscroft, P.; Safiulla, S.; Thirlwall, M. F. *Water Resour. Res.* **2001**, *37*, 109–117.
- Kinniburgh, D. G.; Smedley, P. L. *Arsenic Contamination of Groundwater in Bangladesh*; Technical Report WC/00/19; British Geological Survey: Keyworth, U.K., 2001; Vol. 1–4.
- <http://www.bgs.ac.uk/arsenic/Bangladesh/Data/SpecialStudy-Data.csv>.
- Runkel, R. L.; Kimball, B. A.; McKnight, D. M.; Bencala, K. E. *Water Resour. Res.* **1999**, *35*, 3829–3840.
- Goldberg, S. *Adv. Agron.* **1992**, *47*, 233–329.
- Larsen, F.; Postma, D. *Environ. Sci. Technol.* **1997**, *31*, 2589–2595.
- Stollenwerk, K. G. *Water Resour. Res.* **1998**, *34*, 2727–2740.
- Davis, J. A.; Coston, J. A.; Kent, D. B.; Fuller, C. C. *Environ. Sci. Technol.* **1998**, *32*, 2820–2828.
- Kent, D. B.; Abrams, R. H.; Davis, J. A.; Coston, J. A.; LeBlanc, D. R. *Water Resour. Res.* **2000**, *36*, 3411–3425.
- Appelo, C. A. J.; Drijver, B.; Hekkenberg, R.; De Jonge, M. *Ground Water* **1999**, *37*, 811–817.
- Benjamin, M. M.; Sletten, R. S.; Bailey, R. P.; Bennett, T. *Water Res.* **1996**, *30*, 2609–2620.
- Allison, J. D.; Brown, D. S.; Novo-Gradac, K. J. *MINTEQA2 User Guide*, version 3.11; U.S. EPA: Athens, GA, 1991.
- Parkhurst, D. L.; Appelo, C. A. J. *User's Guide to PHREEQC*, version 2; U.S. Geological Survey Water Resource Inv. 99-4259; 1999.
- Dzombak, D. A.; Morel, F. M. M. *Surface Complexation Modeling—Hydrous Ferric Oxide*; Wiley: New York, 1990.
- Russell, J. D.; Paterson, E.; Fraser, A. R.; Farmer, V. C. *J. Chem. Soc., Faraday Trans.* **1975**, *71*, 1623–1630.
- Evans, T. D.; Leal, J. R.; Arnold, P. W. *J. Electroanal. Chem.* **1979**, *105*, 161–167.
- Zeltner, W. A.; Anderson, M. A. *Langmuir* **1988**, *4*, 469–474.
- Lumsdon, D. G.; Evans, L. J. *J. Colloid Interface Sci.* **1994**, *164*, 119–125.
- Renhart, J. L.; Honeyman, B. D. *Geochim. Cosmochim. Acta* **1999**, *63*, 2891–2901.
- Su, C. M.; Suarez, D. L. *Clays Clay Miner.* **1997**, *45*, 814–825.
- Wijnja, H.; Schulthess, C. P. *Soil Sci. Soc. Am. J.* **2001**, *65*, 324–330.
- Zachara, J. M.; Girvin, D. C.; Schmidt, R. L.; Resch, C. T. *Environ. Sci. Technol.* **1987**, *21*, 589–594.
- Van Geen, A.; Robertson, A. P.; Leckie, J. O. *Geochim. Cosmochim. Acta* **1994**, *58*, 2073–2086.
- Waite, T. D.; Davis, J. A.; Payne, T. E.; Waychunas, G. A.; Xu, N. *Geochim. Cosmochim. Acta* **1994**, *58*, 5465–5478.
- Ostergren, J. D.; Trainor, T. P.; Bargar, J. R.; Brown, G. E.; Parks, G. A. *J. Colloid Interface Sci.* **2000**, *225*, 466–482.
- Bargar, J. R.; Reitmeyer, R.; Lenhart, J. J.; Davis, J. A. *Geochim. Cosmochim. Acta* **2000**, *64*, 2737–2749.
- Wijnja, H.; Schulthess, C. P. *Soil Sci. Soc. Am. J.* **2000**, *64*, 898–908.
- Davis, J. A.; James, R. O.; Leckie, J. O. *J. Colloid Interface Sci.* **1978**, *63*, 480–499.
- Villalobos, M.; Leckie, J. O. *Geochim. Cosmochim. Acta* **2000**, *64*, 3787–3802.
- Villalobos, M.; Leckie, J. O. *J. Colloid Interface Sci.* **2001**, *235*, 15–32.
- Davis, J. A.; Kent, D. B. *Rev. Mineral.* **1990**, *23*, 177–260.
- Zhang, Y.; Charlet, L.; Schindler, P. W. *Colloids Surf.* **1992**, *63*, 259–268.
- Coughlin, B. R.; Stone, A. T. *Environ. Sci. Technol.* **1995**, *29*, 2445–2455.
- Liger, E.; Charlet, L.; Van Cappellen, P. *Geochim. Cosmochim. Acta* **1999**, *63*, 2939–2955.
- Welch, A. H.; Lico, M. S. *Appl. Geochem.* **1998**, *13*, 521–539.
- Welch, A. H.; Westjohn, D. B.; Helsel, D. R.; Wanty, R. B. *Ground Water* **2000**, *38*, 589–604.
- <http://members.ozemail.com.au/~wcomp/index.html>.
- Manseau, A. *Geochim. Cosmochim. Acta* **1995**, *59*, 3647–3653.
- Hiemstra, T.; Van Riemsdijk, W. H. *J. Colloid Interface Sci.* **1996**, *179*, 488–508.
- Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press: New York, 1984.
- Rietra, R. P. J. J.; Hiemstra, T.; Van Riemsdijk, W. H. *Geochim. Cosmochim. Acta* **1999**, *63*, 3009–3015.
- Mathur, S. S. M.Sc. Thesis, Department of Civil Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA, 1995; 178 pp.

- (44) Waychunas, G. A.; Rea, B. A.; Fuller, C. C.; Davis, J. A. *Geochim. Cosmochim. Acta* **1993**, *57*, 2251–2269.
- (45) Manning, B. A.; Fendorf, S. E.; Goldberg, S. *Environ. Sci. Technol.* **1998**, *32*, 2383–2388.
- (46) Charlet, L.; Silvester, E.; Liger, E. *Chem. Geol.* **1998**, *151*, 85–93.
- (47) Fuller, C. C.; Davis, J. A.; Waychunas, G. A. *Geochim. Cosmochim. Acta* **1993**, *57*, 2271–2282.
- (48) Meng, X.; Bang, S.; Korfiatis, G. P. *Water Res.* **2000**, *34*, 1255–1261.
- (49) Wilkie, J. A.; Hering, J. G. *Colloids Surf. A* **1996**, *107*, 97–110.
- (50) Kim, M.-J.; Nriagu, J.; Haack, S. *Environ. Sci. Technol.* **2000**, *34*, 3094–3100.
- (51) Manning, B. A.; Goldberg, S. *Soil Sci. Soc. Am. J.* **1996**, *60*, 121–131.
- (52) Hiemstra, T.; Van Riemsdijk, W. J. *Colloid Interface Sci.* **1999**, *210*, 182–193.
- (53) Swedlund, P. J.; Webster, J. G. In *Water–Rock Interaction*; Arehart, Hulston, Eds.; Balkema: Rotterdam, The Netherlands, 1998; Vol. 9, pp 947–950.
- (54) Kinniburgh, D. Personal communication, 2000.

Received for review May 7, 2001. Revised manuscript received March 5, 2002. Accepted March 18, 2002.

ES010130N