Environ. Sci. Technol. **2007**, *41,* 3660−3666

Modeling the Transport of Metals with Rate-Limited EDTA-Promoted Extraction and Dissolution during EDTA-Flushing of Copper-Contaminated Soils

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EDTA-flushing of artificially contaminated soils enhanced Cu extraction but also induced mineral dissolution simultaneously. The mobilization and transport of these metal−EDTA complexes was investigated with column experiments. A quantitative transport model was proposed for simulating the experimental breakthrough curves of Cu, Fe, Al, and Ca. The rate-limited EDTA-promoted extraction and dissolution could be described by respective second-order kinetic terms, which were necessary for explaining the time-dependent depletion of extractable metals (sorbed and indigenous) in soils with continuous EDTA-flushing. Simultaneous simulation of extraction of sorbed Cu and dissolution of soil Fe, Al, and Ca is more conceptually accurate than individual modeling of each metal because the latter approach tends to overestimate the concentration of free EDTA during transport and thus underestimate the rate coefficients of EDTA-promoted dissolution. The fitted rate coefficients of Cu were about an order of magnitude larger than those of Fe and Al; these values probably reflect Cu extraction from weakly sorbed fractions and Fe and Al dissolution from amorphous oxides. The apparent retardation of Fe, Al, and Ca transport had to be taken into account by empirical determination, which was attributed to the metal lability in soils and thermodynamics of surface complexation.

Introduction

A number of previous studies have demonstrated the capability of EDTA (ethylenediaminetetraacetic acid) in soil washing/flushing for extracting strongly sorbing metal ions from soils via formation of metal−EDTA complexes (*1*−*4*). However, EDTA is also recognized to concurrently complex with soil components such as Fe and Al oxides, aluminosilicates, and carbonates, resulting in their dissolution (*2*, *5*, *6*) and competitive phenomenon among metals in soils (*7*, *8*). Such mineral dissolution can be delineated as a result of EDTA-promoted dissolution, which is initiated by a fast adsorption of free or complexed EDTA onto specific surface sites via surface complexation and followed by a rate-limiting metal detachment from the mineral structure (*9*, *10*). Along with mineral dissolution, some soil organic matter was mobilized and its conformation was probably modified (*11*, *12*). Dissolution would reduce shear strength and aggregate stability of soils (*13*), resulting in mobilization of colloids and clay-size particles (*3*). Moreover, the high mobility of metal−EDTA complexes in the subsurface environment can induce further mineral dissolution together with metal readsorption (*14*, *15*), or remobilization of sorbed metals (*16*) of an extended soil region.

Knowing the speciation of chelating agents, which is governed by slow metal-exchange reactions, is therefore crucial for understanding their environmental fate in natural waters (*17*). A quantitative transport model that is able to describe the mobilization of metal−EDTA complexes can better evaluate the effectiveness and influences of chemical-enhanced flushing. However, only limited modeling efforts have been made. The simulation of metal−EDTA complex transport can be performed using advection−dispersion equations with adjunction of a kinetic sink/source term to express the EDTA extraction reaction (*18*, *19*). Description of the transport data using the kinetic expression of EDTA extraction was shown to be more accurate than using the equilibrium expression (*18*). The transport equations incorporating a second-order kinetic sink/source term can account for the diminishing metal extraction efficiency with the depletion of metal in soils (*19*). Because the existing model focuses on the metal extractability for remediation purposes, it considers the interaction of EDTA with only one metal at a time, neglecting the competition of other metals in soils for EDTA complexation (*19*). Thus, it may not describe the simultaneous mobilization of EDTA complexes of Fe, Al, and Ca resulting from EDTA-promoted dissolution of soil minerals.

Another model was proposed in order to investigate the transport of metal−EDTA complexes in an aquifer where several metal−EDTA complexes and free EDTA (i.e., uncomplexed with metals) were injected (*20*). A series of chemical reactions for dissolution of Fe and Al oxides by metal−EDTA complexes and free EDTA was incorporated into the transport equation, assuming that Fe dissolution is rate-limited while other reactions are in equilibrium. The Fe dissolution kinetics was considered to be pseudo-first-order with respect to the concentrations of free EDTA or metal−EDTA complexes. The simulation results of the mobility of metal−EDTA complexes agreed well with the experimental data of small-scale tracer tests using pulse injection. However, describing dissolution with first-order kinetics may have limited applicability for step input of EDTA, in which extractable soil minerals are probably depleted with continuous EDTA-flushing. Besides, for the transport time scale on the order of hours in this study, EDTA-promoted dissolution of soil minerals is likely to be rate-limited according to previous kinetic studies (*9*, *10*). Thus, kinetics of mineral dissolution of Al and Ca may also have to be taken into account for metal−EDTA complex transport.

This paper extends previous transport models to improve understanding of the transport of metal−EDTA complexes during EDTA-flushing, accounting for simultaneous, rate-limited, EDTA-promoted extraction of the target metal and dissolution of soil minerals (i.e., Cu, Fe, Al, and Ca). The model simulations were compared with the data of column experiments using artificially Cu-contaminated soils under different contaminations (low and high Cu loadings and aged) and operation conditions (two pore-water velocities). EDTA was employed as a reference compound, which could provide

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10.1021/es061756m CCC: $37.00

relevant insights for the recently proposed use of easily biodegradable chelating agents (e.g., *S*,*S*-ethylenediaminedisuccinic acid (SS-EDDS) (*21*)) in soil washing/flushing (*6*, *22*, *23*) and phytoextraction (*24*, *25*).

Experimental Section

Soil Characteristics. An uncontaminated soil sample, taken from 25−50 cm below ground surface at the campus of Hong Kong University of Science and Technology in Hong Kong, was air-dried and passed a 2-mm sieve. The soil was comparable to sandy loam (64% sand, 20% silt, 16% clay by mass) according to particle-size distribution obtained by sieving and hydrometer methods. The organic and inorganic carbon contents were 1.47% and 0.14%, measured by a total organic carbon analyzer with solid sample module (Shimadzu TOC-5000A) using an infrared spectrometer after combustion in a furnace (total carbon) and acidification (total inorganic carbon). The soil pH was 7.6, measured at a 1:2 soil-to-water ratio. Measured by nitrogen gas adsorption (Micromeritics ASAP2010), the soil possessed BET surface area of 7.04 m^2 g^{-1} and unnoticeable micropore surface area. The cation exchange capacity (CEC) of the soil was 34.9 meq per 100 g, measured by NH_4−Na exchange. The most abundant mineral was kaolinite, determined by X-ray diffraction (XRD) analysis of clay-size particles. The relative mass percentages of metals in the soil were 5.98% Fe, 25.0% Al, 3.07% Ca, and 0.355% Mn, as measured by X-ray fluorescence (XRF) spectrometry (JEOL JSX-3201Z). The concentrations of amorphous Fe/Al/Mn oxides, determined using ammonium oxalate extraction, were 6.06 ± 0.04, 17.6 ± 0.2, and 0.835 ± 0.016 mmol kg^{-1}, respectively. The total amounts (crystalline and amorphous) of Fe/Al/Mn oxides, determined by dithionite−carbonate−bicarbonate (DCB) extraction, were 112 ± 2, 29.5 ± 0.6, and 2.25 ± 0.07 mmol kg^{-1}, respectively. Therefore, most of the Fe oxides (~95%) present in this soil are crystalline. It has been shown that Mn dissolution could be significant in some soils because its stability constant for complexation is even higher than that of Ca (*5*, *23*). However, the amount of Mn oxides was much smaller than that of Fe/Al oxides in this soil, as shown by XRF and oxalate/DCB extractions. Preliminary 3-d batch extraction experiments (5:1 EDTA−metal molar ratio) and column experiments showed insignificant Mn dissolution. Hence, Mn dissolution was not a further concern.

Experiments. Column experiments were performed in 3.6-cm internal diameter, 10-cm long columns at 10 ± 0.5 °C to simulate the subsurface temperature. The columns were packed in small incremental steps with the soil to obtain a uniform bulk density of 1.508 g cm^{-3}, corresponding to a porosity of 0.433. Filter papers (0.45-μm nominal pore size) were placed at the ends of the soil columns to ensure the effluent free of turbidity. The soil columns were oriented vertically and slowly saturated with an upward-flowing background solution (0.03 M $NaNO_3$ at pH 5) to prevent the formation of metal precipitates and maintain a stable ionic strength. A portion of Ca carbonates was dissolved during the early stage of soil conditioning. Copper was the studied contaminant because it is one of the heavy metals most often encountered in contaminated sites (*26*). Soils of different metal loadings and contamination aging, which probably influence EDTA extraction efficiency (*27*, *28*), were prepared for EDTA-flushing. The soil columns were artificially contaminated by leaching with background solution containing 10 and 100 mg L^{-1} of $Cu(NO_3)_2$, respectively, until the influent and effluent Cu concentrations were approximately equal. The corresponding low and high Cu loadings in the soil measured by microwave digestion were 4.99 ± 0.16 and 15.8 ± 0.9 mmol kg^{-1}, which cover the normally encountered range of contamination. Negligible dissolution of Fe, Al, Ca, and organic matter was observed during Cu contamination.

Aged contamination was prepared by sealing the soil columns of high Cu loading to maintain water saturation for 9 months. The initial pH of the effluent after aging (3.9−4.4) was lower than that of freshly contaminated soils (4.5−5.3), probably indicating a greater extent of specific sorption of Cu via inner-sphere complexation with oxides and organic matter (*29*, *30*). This was supported by the preliminary sequential extraction results, which showed a larger portion of organic matter fraction at low Cu loading and a redistribution of sorbed Cu from exchangeable and carbonate (weakly bound) fractions to oxide and organic matter (strongly bound) fractions upon aging. The aging effect on EDTA extraction was also reflected by the reduction of the extractable Cu amount (Supporting Information Table S1).

Following Cu contamination, the soil columns were fed with the background solution for 1−2 pore volumes to leach loosely entrapped Cu, and afterward flushed with the EDTA solution of 10^{-3} M or 10^{-2} M in view of the previous studies (*3*−*5*, *19*). The EDTA solution was prepared by dissolving appropriate amounts of disodium salt of EDTA (Na_2EDTA) into solution of $NaNO_3$ maintaining a constant ionic strength of 0.03 M and pH 5. Flushing was applied at a pore-water velocity of 17.53 ± 1.2 cm h^{-1}, except that two of the aged columns employed slow flushing at 8.02 ± 0.15 cm h^{-1}. The effluent pH of all soil columns approached about 5 during EDTA-flushing. EDTA extraction efficiency of Cu is pH-independent in the range of 4−6 given that there is free EDTA remaining in solution (*6*, *31*), which was valid for the step input of EDTA in this study. Effluent samples were collected periodically throughout the course of the experiments. The dissolved Cu, Fe, Al, and Ca concentrations in the effluent were analyzed by atomic absorption spectrometry (Hitachi Z-8200) and plotted versus flushing pore volume to construct the breakthrough curves (BTCs). A 16-h flow interruption was performed, when the effluent Cu concentration nearly leveled off, to determine any kinetic limitation of EDTA extraction.

The (maximum) EDTA-extractable amounts (mmol kg^{-1}) of metals in soils were estimated by 3-day batch experiments, in which the metals (Cu, Fe, Al, and Ca) were extracted from 15 g of Cu-contaminated soils by 0.5 L of 10^{-2} M EDTA solution or 1 L of 10^{-3} M EDTA solution, respectively. These ratios approximately corresponded to the ratios of soil amount in column to total flushing volume. The results (Supporting Information, Table S1) indicated that the extractable amount of Cu was mainly influenced by the contamination condition while those of Fe, Al, and Ca were virtually dependent on the EDTA concentration.

To determine the hydrodynamic characteristics of the columns, bromide solution (10 mg L^{-1} NaBr) was introduced into the soil columns together with EDTA and analyzed by ion chromatography (Dionex DX-500). The Br BTCs (not shown) exhibiting a symmetrical and sharp breakthrough suggested an absence of immobile water region. The hydrodynamic dispersion coefficient D of each column was determined by optimizing the Br BTCs with equilibrium transport equation. The concentration of dissolved organic carbon, measured by total organic carbon analyzer (Shimadzu TOC-5000A), increased rapidly and rose above the levels corresponding to EDTA concentrations (i.e., 120 and 1200 mg L^{-1} for 10^{-3} and 10^{-2} M, respectively) along with Br breakthrough after 2−3 pore volumes, indicating that the transport of total EDTA was not significantly retarded.

Transport Model. To simulate the transport behavior of metal−EDTA complexes with minimum number of parameters for the sake of practical applicability, this model only takes into account the most influential chemical reactions (complexation) between metals and chelants during EDTA-flushing. They include the extraction of sorbed Cu and dissolution of Fe and Al oxides and Ca carbonates, largely promoted by free EDTA (H_2EDTA^{2-} is the dominant species across the pH range of this study) forming 1:1 metal−EDTA complexes.

$$>\mathrm{SOCu}^{+} + \mathrm{H_2EDTA}^{2-} \rightarrow \mathrm{CuEDTA}^{2-} + >\mathrm{SOH} + \mathrm{H}^{+} \tag{1}$$

$$\mathrm{Fe(OH)_3} + \mathrm{H_2EDTA}^{2-} + \mathrm{H}^{+} \rightarrow \mathrm{FeEDTA}^{-} + 3\mathrm{H_2O} \tag{2}$$

$$\mathrm{Al(OH)_3} + \mathrm{H_2EDTA}^{2-} + \mathrm{H}^{+} \rightarrow \mathrm{AlEDTA}^{-} + 3\mathrm{H_2O} \tag{3}$$

$$\mathrm{CaCO_3} + \mathrm{H_2EDTA}^{2-} \rightarrow \mathrm{CaEDTA}^{2-} + \mathrm{CO_2} + \mathrm{H_2O} \tag{4}$$

where $>\mathrm{SO}^-$ represents metal sorption sites on soil surface, such as hydroxyl groups at the edge of clay minerals and functional groups of organic matter. It should be noted that Ca dissolution from carbonate and/or cation exchange sites are lumped together (eq 4). The prime significance of EDTA-promoted dissolution during EDTA-flushing was justified by negligible Fe and Al dissolution and far less Cu extraction by flushing with background solution in preliminary experiments. However, proton-promoted dissolution of Ca was important during the early stage of EDTA-flushing of soils with aged contamination that reduced the solution pH to about 4, which cannot be explained by the above equations.

For the simplicity of modeling the transport behavior, the possible reactions (remobilization/dissolution) by metal−EDTA complexes are assumed negligible compared with the reactions by free EDTA (eqs 1−4), which are the most kinetically significant reactions. Previous studies demonstrated that rate coefficients for Fe-oxide dissolution kinetics were in the order of free EDTA > $AlEDTA^-$, $CaEDTA^{2-}$ > $CuEDTA^{2-}$ (*9*), and Al-oxide dissolution kinetics was much faster when mediated by free EDTA than $CaEDTA^{2-}$ (*20*). Besides, for continuous EDTA-flushing, the dominance of the reactions by free EDTA (eqs 1−4) was justified by mass balance calculation. The sum of molar concentrations of metals (Cu, Fe, Al, and Ca) in the effluent was smaller than injected molar concentration of EDTA all the time, which means free EDTA is always present in the flushing solution.

In view of previous observation of a slow metal extraction kinetics following an initial fast release in batch studies (*6*, *31*, *32*) and the reported time scale of EDTA-promoted dissolution (*9*, *10*), Cu extraction and Fe/Al/Ca dissolution were described with kinetic terms, in turn incorporated into advection−dispersion equations (ADEs). This model extended the proposed framework of Kedziorek et al. (*19*).

For the transport of free EDTA, several kinetic sink terms were included in the ADE to account for the formation of metal−EDTA complexes of Cu, Fe, Al, and Ca, respectively.

$$\frac{\partial C_E}{\partial t} = D\frac{\partial^2 C_E}{\partial z^2} - v\frac{\partial C_E}{\partial z} + \frac{\partial C_{M,Cu}}{\partial t} + \frac{\partial C_{M,Fe}}{\partial t} + \frac{\partial C_{M,Al}}{\partial t} + \frac{\partial C_{M,Ca}}{\partial t} \tag{5}$$

where v is the pore-water velocity (cm h^{-1}); D is the hydrodynamic dispersion coefficient ($cm^2\ h^{-1}$); C_E is the free EDTA concentration in solution (mmol L^{-1}); $C_{M,j}$ (j = Cu, Fe, Al, Ca, respectively) are the extractable concentrations of metals in soils (mmol L^{-1}); and $\partial C_{M,j}/\partial t$ are the kinetic sink terms for free EDTA transport.

To simulate the transport of metal−EDTA complexes, respective kinetic source terms were included in the ADE of each metal to account for the formation of metal−EDTA complexes.

$$R_j\frac{\partial C_{EM,j}}{\partial t} = D\frac{\partial^2 C_{EM,j}}{\partial z^2} - v\frac{\partial C_{EM,j}}{\partial z} - \frac{\partial C_{M,j}}{\partial t} \quad (j = \mathrm{Cu, Fe, Al, Ca, respectively}) \tag{6−9}$$

where $C_{EM,j}$ are the concentrations of complexed metals in solution (mmol L^{-1}); R_j are the apparent retardation factors (dimensionless) for each metal−EDTA complex; and $\partial C_{M,j}/\partial t$ are the kinetic source terms for respective metal−EDTA complex transport.

The kinetic sink/source terms ($\partial C_{M,j}/\partial t$), which represent eqs 1−4 to account for the formation of metal−EDTA complexes in the ADEs (eqs 5−9), can be described with second-order kinetics (i.e., first-order with respect to the free EDTA concentration in solution and first-order with respect to the extractable concentration of metals in soils). In addition to the consideration of competitive EDTA-promoted dissolution of Fe, Al, and Ca, the formulation differs from the previous one (*19*) in a way that the extractable level of metals (mmol L^{-1}), instead of the extractable fraction of metals, is taken into account.

$$\frac{\partial C_{M,j}}{\partial t} = -k_j C_E C_{M,j} \quad (j = \mathrm{Cu, Fe, Al, Ca, respectively}) \tag{10−13}$$

where k_j (L mol^{-1} s^{-1}) are the rate coefficients of EDTA-promoted extraction (i.e., Cu) or dissolution (i.e., Fe, Al, and Ca). Despite involvement of hydrogen ion concentration in eqs 1−4, it is assumed relatively constant and incorporated in the rate coefficients (*20*).

The simulations of transport of metal−EDTA complexes were performed using a finite difference method to solve eqs 5−9 (advection and sink/source terms were solved explicitly with upstream weighting; dispersion term was solved implicitly), with appropriate initial and boundary conditions. Initial values of $C_{M,j}$ (j = Cu, Fe, Al, Ca) were calculated by dividing the product of batch-measured extractable amounts (mmol kg^{-1}) and bulk density (kg L^{-1}) by column porosity (dimensionless). The rate coefficients k_j were adjusted to fit the experimental data of each metal−EDTA complex transport.

For reactions 1−4 initiated by free EDTA, the reaction kinetics represents the rate-limiting detachment of metal−EDTA complex from the surface depending on the concentration of the prior activated surface complex formation (*9*, *10*). In addition to the second-order formulations (eqs 10−13), the kinetic expression may be described as pseudo-first-order with respect to the concentration of EDTA, as employed by Friedly et al. (*20*), which implicitly assumed that the amounts of extractable metals in soils are comparatively in excess. Because the results of soil characterization showed relatively abundant amounts of Fe, Al, and Ca compared with Cu in soils, the appropriateness of first-order kinetics for Fe, Al, and Ca dissolution was also assessed.

The hydrodynamic dispersion coefficient was determined by modeling the Br transport and assumed to be constant irrespective of metal−EDTA complexes, because preliminary modeling efforts revealed the simulation is relatively insensitive to dispersion coefficient. On the other hand, knowing that the transport behaviors and elution times of different metals are probably different, as observed in previous studies (*2*, *5*), an apparent retardation factor is assigned to each metal−EDTA complex so as to describe the corresponding retarded breakthrough. The values of R were empirically determined by dividing the pore volume of respective metal peaks by that of Br peak. Preliminary simulations without

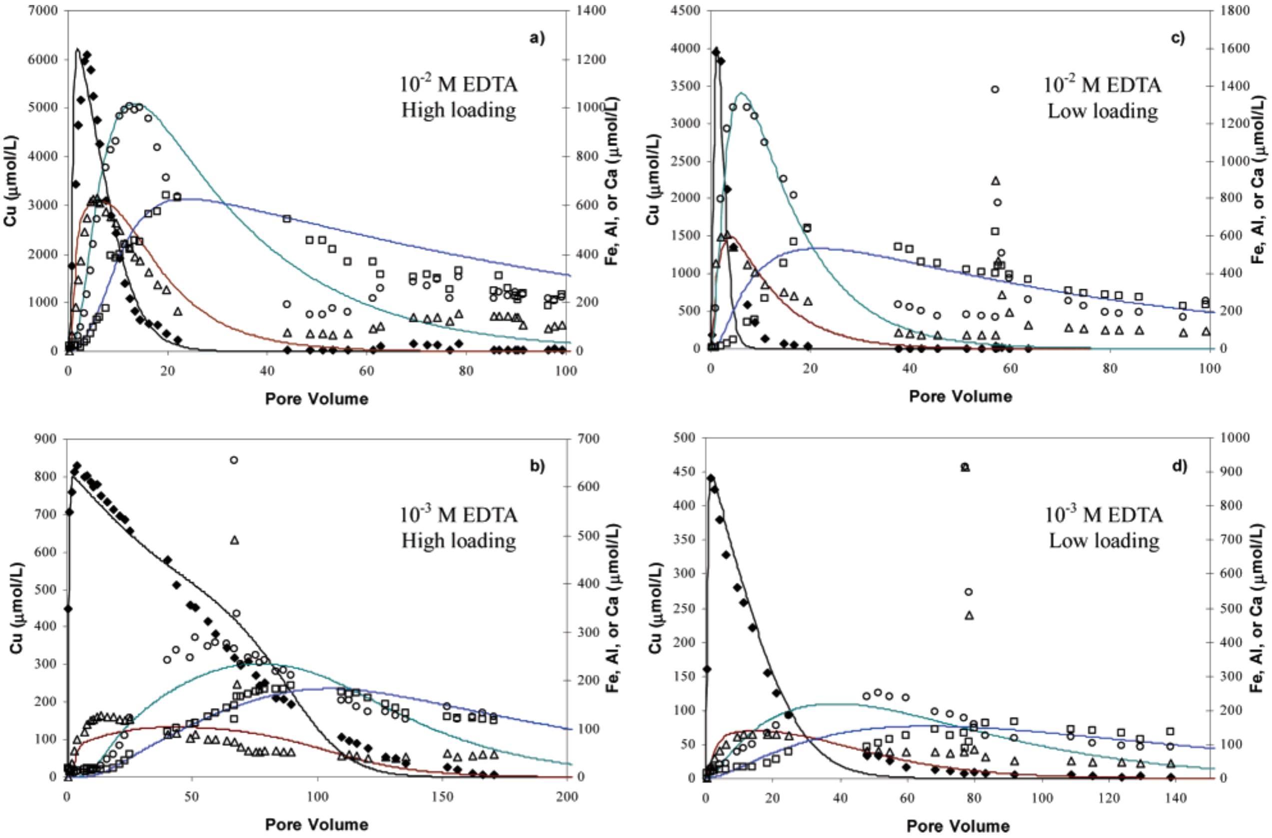

FIGURE 1. Breakthrough curves of Cu, Fe, Al, and Ca during EDTA-flushing of soils: (a) 10^{-2} M EDTA, high Cu loading; (b) 10^{-3} M EDTA, high Cu loading; (c) 10^{-2} M EDTA, low Cu loading; (d) 10^{-3} M EDTA, low Cu loading (◆ Cu; △ Fe; ○ Al; □ Ca; lines represent respective model simulations; obvious increase of concentrations in b–d upon 16-h flow interruption).

apparent retardation (i.e., $R = 1$ for all complexes) failed to match with the experimental BTCs.

Results and Discussion

Simulation of Simultaneous Transport of Metal–EDTA Complexes. EDTA-flushing significantly enhanced the Cu extraction while it induced simultaneous transport of metal–EDTA complexes of Fe, Al, and Ca from soils under different contamination and operation conditions. The simultaneous transport of metal–EDTA complexes is illustrated in Figures 1 and 2. Upon flow interruption, perturbation of Cu (Supporting Information Figure S1) and Fe and Al concentrations (Figure 1b, c, d), in line with previous findings (*14*, *15*), suggested that EDTA-promoted dissolution should be rate-limited and described by kinetic expression in transport modeling. In general, flushing of lower EDTA concentration resulted in lower and flatter peaks, underlining the dependence of dissolution kinetics on EDTA concentration.

The Cu peaks emerging closely together with the Br peaks indicated that Cu–EDTA complex was not obviously retarded. The apparent retardation factor of Cu transport was thus set equal to unity for all simulations. The fitted rate coefficients of Cu transport multiplying by metal concentrations of soils were on the order of 10^{-4} to 10^{-3} s^{-1} (Supporting Information Table S2), which were larger than previously reported first-order rate coefficients (on the order of 10^{-5} s^{-1}) (*19*, *33*). This is probably because the predominant fractions of soil Cu were weakly sorbed due to relatively high metal loadings (4.989–15.784 mmol kg^{-1}) and artificial contamination. In addition, compelling inference cannot be drawn on the impact of slow and fast flushing and different contamination conditions.

The model that considers Cu transport singly was evaluated (Supporting Information Figure S1) but it led to the rate coefficients of Cu transport smaller than those obtained by considering the simultaneous complexation with EDTA between sorbed Cu and soil minerals (1.7×10^{-2} to 1.0×10^{-1} L mol^{-1} s^{-1}), as shown in Table 1. It should be noted that the transport of free EDTA (eq 5) was influenced by all sink terms (eqs 10–13) resulting from the EDTA-promoted dissolution (eqs 1–4). A negligence of the metal–EDTA complexes originating from soil minerals and the corresponding sink terms (i.e., assuming all non-Cu complexed EDTA is free EDTA) would overestimate the concentration of free EDTA during transport, thereby underestimating the rate coefficients of EDTA-promoted dissolution as observed. This clearly points to the significance of considering mineral dissolution simultaneously. Similarly, the rate coefficients would be underestimated if each of multiple metal contaminants in soils competing for EDTA complexation is considered individually, and the underestimation would be more significant for reaction kinetics of similar magnitude.

The first-order kinetics was found inadequate for continuous EDTA-flushing, because besides sorbed Cu, soil Fe, Al, and Ca that can be extracted by EDTA were depleted. This is illustrated in Supporting Information Figures S2 and 3, where the first-order kinetic model only simulated gradual increase of metal dissolution that eventually reached plateau with continuous flushing. EDTA-promoted dissolution is initiated by ligand adsorption to the specific surface sites of minerals that polarizes the critical metal–oxygen bonds and enhances the detachment of the metal center from the crystal structure (*9*, *10*). Therefore, the dissolution kinetics that is dependent on the concentration of the activated surface complex should be in turn a function of both EDTA concentration and extractable amount of metals in soil matrix (i.e., amount of specific surface sites), as described by eqs 11–13.

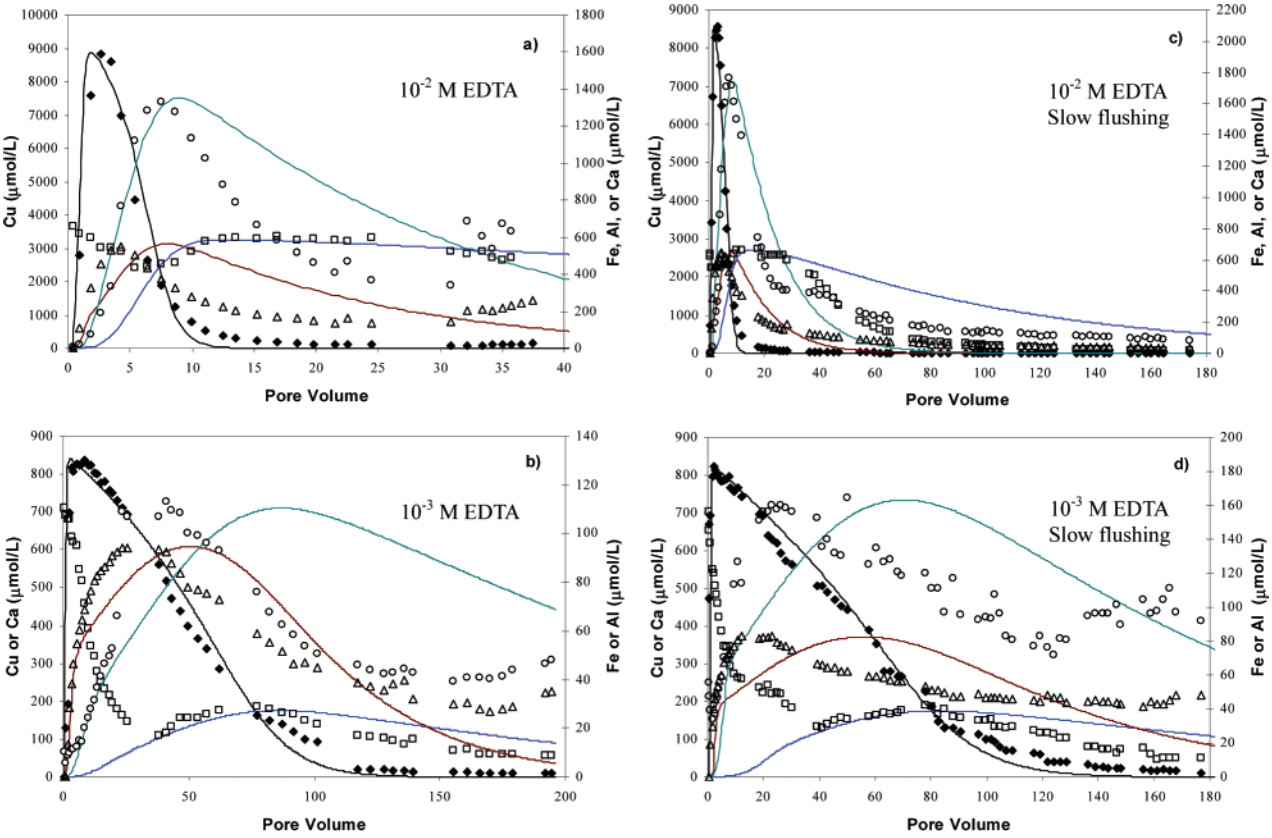

FIGURE 2. Breakthrough curves of Cu, Fe, Al, and Ca during EDTA-flushing of soils with aged Cu contamination: (a) 10^{-2} M EDTA; (b) 10^{-3} M EDTA; (c) slow flushing of 10^{-2} M EDTA; (d) slow flushing of 10^{-3} M EDTA (◆ Cu; △ Fe; ○ Al; □ Ca; lines are respective model simulations).

TABLE 1. Second-Order Rate Coefficients (L mol^{-1} s^{-1}) and Apparent Retardation Factors for EDTA-Promoted Extraction of Cu and Dissolution of Fe, Al, and Ca during EDTA-Flushing

	Low Cu Loading		High Cu Loading		Aged Contamination			
					10^{-3} M EDTA		10^{-2} M EDTA	
	10^{-3} M EDTA	10^{-2} M EDTA	10^{-3} M EDTA	10^{-2} M EDTA		Slow flushing		Slow flushing
Optimizing Cu alone								
Cu	5.1×10^{-2}	4.8×10^{-2}	2.0×10^{-2}	1.25×10^{-2}	2.3×10^{-2}	9.0×10^{-3}	3.2×10^{-2}	1.5×10^{-2}
Optimizing Cu, Fe, Al, and Ca together								
Cu	1.0×10^{-1}	6.7×10^{-2}	8.0×10^{-2}	1.7×10^{-2}	5.4×10^{-2}	2.3×10^{-2}	5.7×10^{-2}	3.0×10^{-2}
Fe	3.3×10^{-2}	5.8×10^{-3}	3.2×10^{-2}	5.3×10^{-3}	1.4×10^{-2}	4.6×10^{-3}	3.1×10^{-3}	2.0×10^{-3}
Al	1.5×10^{-2}	4.5×10^{-3}	1.5×10^{-2}	2.3×10^{-3}	3.3×10^{-3}	2.7×10^{-3}	2.3×10^{-3}	1.7×10^{-3}
Ca	6.4×10^{-3}	7.2×10^{-4}	5.5×10^{-3}	5.7×10^{-4}	4.5×10^{-3}	2.0×10^{-3}	4.3×10^{-4}	2.5×10^{-4}
Apparent Retardation Factor[a]								
R_{Fe}	4.20	1.20	3.96	1.76	3.98	3.29	1.32	1.46
R_{Al}	19.2	4.12	19.8	6.68	11.7	6.50	2.89	2.30
R_{Ca}	34.5	14.5	26.4	11.8	25.7	24.3	5.21	5.70

[a] Apparent retardation factors were empirically determined by respective ratios of pore volumes of metal peaks relative to Br peak.

The second-order rate coefficients of Fe, Al, and Ca transport were in the ranges of 2×10^{-3} to 3.3×10^{-2}, 1.7×10^{-3} to 1.5×10^{-2}, and 2.5×10^{-4} to 6.4×10^{-3} L mol^{-1} s^{-1}, respectively (Table 1). The rate coefficients of Fe and Al dissolution were about 1 order of magnitude smaller than those of Cu extraction, while an order of magnitude larger than those of Ca dissolution. But when the first-order rate coefficients were considered, in which the effect of difference in extractable amounts of metals (Supporting Information Table S1) was excluded, the kinetics of Fe, Al, and Ca dissolution were comparable and about an order of magnitude slower than that of Cu (on the order of 10^{-5} to 10^{-4} s^{-1}, Supporting Information Table S2). The rate coefficients of Fe and Al dissolution were large compared with the reported values for crystalline minerals (*10*), suggesting that the observed dissolution should mainly derive from amorphous Fe and Al oxides, which has a much faster kinetics than crystalline oxides (*9*). This seems to be reasonable as the extractable amounts of Fe and Al did not exceed their respective amorphous amounts (Supporting Information Table S1). In addition, sharper peaks at higher EDTA concentration (Figure 1) reflected the faster overall kinetics of Fe, Al, and Ca dissolution. Slow flushing enhanced Al dissolution but not Fe dissolution (Figure 2), implying that the former is more dependent on the transport time scale on the order of hour whereas the kinetics of Fe dissolution may be on the order of day.

The initial Ca dissolution after contamination aging that brought the pH to 3.9−4.4 was most likely proton-promoted (corresponding to <10 and 40 pore volumes in Figures 2a and c and 3b and d, respectively), because this was similarly observed in the absence of EDTA. The later Ca dissolution was EDTA-promoted that could be simulated with the model (Figure 2). The early dissolved Ca would form Ca−EDTA complex in solution, which is less effective in mediating Fe and Al dissolution than free EDTA (*9*, *20*), probably responsible for a lesser extent of Fe and Al dissolution at early stage (comparing Figures 1a and 2a, and 1b and 2b). On the other hand, Fe and Al dissolution from the aged soils (Figure 2) was significantly inhibited after the peak arrivals and their transport was overestimated with the use of single rate coefficient. This was probably attributed to inner-sphere complexation and/or surface precipitation (of less importance) of Cu (*29*, *34*) which could proceed to a greater extent with aging (*35*). Strong metal sorption via inner-sphere complex may inhibit the detachment of Fe or Al from the oxide structure (*10*); formation of surface precipitates that changes lattice geometry of oxides may increase the crystallinity with time (*36*). The readiness and availability of Fe and Al oxides for EDTA-promoted dissolution were consequently reduced. This was corroborated by the amount of cumulative Fe and Al dissolution (Supporting Information Figure S4), which was suppressed particularly at later stage of flushing and lower EDTA concentration.

Apparent Retardation. The apparent retardation factors were fairly constant for each metal under different contamination conditions, while they were smaller at higher EDTA concentration (Table 1). Adsorption of metal−EDTA complexes on Fe and Al oxides is feasible at acidic pH of this study via electrostatic attraction, formation of ternary surface complex (*37*), outer-sphere complexation, or hydrogen bonding (*38*, *39*). However, Cu− and Ca−EDTA complexes should have been more retarded than Fe− and Al−EDTA complexes if adsorption was significant, whereas the order of elution was Cu followed by Fe, then Al, and last Ca. The retarded metal−EDTA complex transport is therefore interpreted as an apparent retardation because it does not predominantly originate from adsorption.

The metal lability, thermodynamics, or dissolution kinetics was suspected to incur the apparent retardation of different metals. In preliminary modeling efforts, the rate coefficients were tremendously reduced to allow the appearance of peaks to delay without apparent retardation factors, which however could not provide adequate simulation curves for the data. Therefore, the rate coefficients of Fe, Al, and Ca (Table 1) reflected the chemical kinetics of the EDTA-promoted dissolution (i.e., rate of detachment of metal−EDTA complex from the surface) more than their relative order of elution.

The metal lability primarily controls its accessibility and availability for EDTA complexation. EDTA complexation with more labile sorbed Cu on soil surface would be preferred to complexation with less labile cations residing in oxide and carbonate structure. Therefore, Cu was first eluted although its stability constant ($\log K_{s,Cu} = 19.7$ (*40*)) is not the greatest among the metal−EDTA complexes. When the metal lability is not significantly different (e.g., amorphous Fe oxides and amorphous Al oxides), the order of dissolution conformed to the stability constants of metal−EDTA complexes (i.e., $\log K_{s,Fe} = 26.5 > \log K_{s,Al} = 17.6 > \log K_{s,Ca} = 11.5$ (*40*)). Because the thermodynamics of complexation determines the preference of soil metals for the instantaneous formation of surface complex with EDTA (the first step of EDTA-promoted dissolution), a metal with a stronger affinity for complexation would be preferentially dissolved. The order of dissolution is consequently the preference of initial surface complexation depending on metal lability and thermodynamics. It is then understandable that the apparent retardation was smaller at higher EDTA concentration.

Model Limitations. Several possible limitations of the model deserve attention and justification beforehand. This model makes use of a single rate coefficient for each reaction for the sake of practical application with minimum parameters. However, a single rate coefficient inevitably lumps different dissolution rates of amorphous and crystalline oxides together, or different extraction rates of weakly and strongly sorbed Cu together. The largest discrepancy between model simulation and data was observed at later flushing, possibly due to the slow dissolution of crystalline oxides. It is therefore desirable to obtain prior knowledge of soil metal forms (e.g., amounts of amorphous and crystalline oxides, and sorbed metal distribution) and their respective dissolution rates.

The kinetics of rate-limited EDTA-promoted extraction and dissolution during transport were taken into account in the model, while metal lability and thermodynamics of surface complexation could not be explicitly incorporated. Consequently, the apparent retardation factors of transport have to be determined empirically. Nevertheless, they were found to be fairly constant and thus the previous results can be referred before model simulations. Regarding the conservation of total EDTA, a reasonably good comparison was obtained between the simulated and observed transport of total EDTA (Supporting Information Figure S5), justifying the adequacy of the proposed model incorporating apparent retardation factors.

Besides, mineral dissolution may destabilize the aggregates and alter the hydrodynamic properties of soils, such as size and distribution of pores and diffusion path. In line with previous studies (*2*, *5*, *23*), clogging was observed at the later stage of 10^{-2} M EDTA-flushing. These physical changes would influence the model accuracy at long elution times.

Supporting Information Available

EDTA-extractable amounts of Cu, Fe, Al, and Ca, calculated first-order rate coefficients, observed and simulated transport of Cu−EDTA complex alone, observed and simulated transport of all metal−EDTA complexes using first-order kinetic model, cumulative amounts of Fe and Al dissolution, and simulated and observed transport of total EDTA. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review July 24, 2006. Revised manuscript received January 2, 2007. Accepted March 19, 2007.

ES061756M