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Competitive Cu and Cd Sorption and Transport in Soils: A Combined Batch Kinetics, Column, and Sequential Extraction Study

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The competitive effect influenced the transport behavior of Cu and Cd contrastingly in soils, as illustrated by the experimental findings obtained from column, batch kinetics, and sequential extraction tests. Of particular interest, Cd transport behavior changed from nonequilibrium in a single-metal system to equilibrium in a binary-metal system, whereas Cu exhibited a slightly greater degree of nonequilibrium transport under competition. The equilibrium time of specific sorption (∼7 days) was found to be much longer than that of nonspecific sorption (∼30 min). While there was a competitive effect on nonspecific sorption for both Cu and Cd, the majority of rate-limited specific sorption of Cd on oxide and organic matter fractions (contributing to ∼20% of total sorption) was dramatically displaced by Cu. Such a strong suppression of specific sorption of Cd by the presence of Cu resulted in a shorter equilibrium time of overall sorption, which probably accounts for its equilibrium transport. In contrast, the competitive effect on rate-limited sorption and transport behavior of Cu was less significant. This study demonstrated a correlation between the competitive effect of Cu and Cd on their nonspecific and specific sorption and the corresponding significance of rate-limited sorption and nonequilibrium transport behavior.

Introduction

The simultaneous presence of several heavy metals is common in contaminated soils. Pollution arising from smelters, agricultural use of sewage sludge, and application of fertilizers usually contains Cu and Cd of comparable amounts (*1, 2*). Cu is more toxic to plants than animals, whereas Cd is particularly toxic to higher animals (*3*). It has been fairly well documented that Cu is preferentially sorbed and less affected by the presence of other heavy metals, while it can depress sorption of comparatively weakly sorbing heavy metals such as Cd, Ni, and Zn (*4, 5*). The selectivity sequence of heavy-metal sorption was found to be related to a few factors, including charge-to-radius ratio, electronegativity, softness parameter, and first hydrolysis constant (*6*−*8*), which reflects that metals are sorbed via different mechanisms on heterogeneous soil components with a range of bonding strength (e.g., from nonspecific to specific) and characteristics (e.g., from electrostatic to covalent).

Recent studies have demonstrated that separate consideration of nonspecific and specific sorption would give better insight into competitive sorption, because the extent of the competitive effect on nonspecific and specific sorption differs. Competition between Pb and Cd appeared to merely inhibit exchangeable sorption, leading to speculation that each specific high-energy sorption site on soils has affinity for a particular heavy metal only (*9*) or that the specific sorption of the metals was promoted despite suppression of overall sorption (*10*). Conversely, specific sorption of Zn was found to be depressed by competition with Cu which was predominantly specifically sorbed on clay minerals, amorphous hydrous oxides, and organic matter (*11, 12*). On the other hand, different degrees of the competitive effect of Al on nonspecific and specific sorption of Pb and Cd to humic acid were successfully described in terms of cation exchange and surface complexation (*13*). However, all of these studies have focused on the competitive sorption of heavy metals in soils under equilibrium conditions using batch sorption experiments.

A few studies investigated the competitive transport of heavy metals in column experiments, for which a forthright expectation would be a reduction in retardation due to competitive sorption. In previous studies of competitive transport of Cd, Zn, and Ni in soils, the position of breakthrough could be described only when both competitive nonspecific cation exchange and competitive specific sorption were taken into account, since specific sorption displayed a lower degree of competition than nonspecific sorption (*14, 15*). Attention thus far has emphasized equilibrium conditions. However, for many prevailing situations where kinetic effects are noticeable, the competitive effect may influence not only the extent of sorption (i.e., retardation of breakthrough) but also the transport behavior of different metals. Since the kinetics of nonspecific and specific sorption are unlikely to be the same, different extents of competition involving nonspecific and specific sorption probably result in a different (apparent) equilibrium time of overall sorption. The rate-limited sorption is known to be one of the major factors contributing to nonequilibrium transport behavior. Given the potential discrepancy of the competitive effect on nonspecific and specific sorption, strongly and weakly sorbing ions (i.e., Cu and Cd) may exhibit vastly different (i.e., equilibrium or nonequilibrium) transport behaviors in the presence and absence of competition.

The purpose of this study was to facilitate our understanding of the competitive effect on sorption kinetics and the corresponding transport behavior. Single- and binary-metal transport behaviors of Cu and Cd in column experiments were evaluated with equilibrium and nonequilibrium transport models. Soil samples of batch kinetics and column experiments were analyzed with a sequential extraction scheme so as to understand the kinetics of nonspecific and specific sorption and their significance under different degrees of the competitive effect.

Experimental Section

Soil. A soil sample, taken from 25−50 cm below ground surface in Hong Kong, was air-dried and passed through 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, and it contained 1.47% organic carbon content, measured by a total organic carbon analyzer (Shimadzu, TOC-5000A) with an infrared spectrometer after combustion in a furnace (total carbon) and acidification (total inorganic carbon). The

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TABLE 1. Parameter Values of Equilibrium and Nonequilibrium Transport Models and Sorbed Amounts of Cu and Cd in Column Experiments Using Various Cu and/ or Cd Loadings

		equilibrium and nonequilibrium transport models				sorbed amount (mmol kg^{-1})[a]		
		D (cm^2 h^{-1})[b]	R[c]	F[d]	α (h^{-1})[d]	Cu or Cd	total (binary)[e]	total (single)[f]
single	10 mg L^{-1} Cu	11.277	187.216	0.864	0.017	10.291 ± 0.426		
single	100 mg L^{-1} Cu	13.223	41.503	0.743	0.019	18.112 ± 0.935		
single	10 mg L^{-1} Cd	9.660	83.222	0.037	0.159	4.977 ± 0.083		
single	100 mg L^{-1} Cd	10.169	31.833	0.664	0.086	10.634 ± 0.136		
single	10 mg L^{-1} Cu	12.533	181.317	0.587	0.019	9.616 ± 0.713	11.154	15.267
	10 mg L^{-1} Cd		61.611	N/A[g]	N/A[g]	1.538 ± 0.091		
Binary	100 mg L^{-1} Cu	10.918	39.083	0.531	0.026	16.693 ± 0.418	20.549	28.747
	100 mg L^{-1} Cd		34.913	N/A[g]	N/A[g]	3.856 ± 0.037		
Binary	10 mg L^{-1} Cu	15.279	140.252	0.363	0.018	8.094 ± 0.578	15.590	20.925
	100 mg L^{-1} Cd		34.913	0.972	2.0E-07	7.496 ± 0.226		
Binary	100 mg L^{-1} Cu	14.030	39.968	0.517	0.027	17.674 ± 0.084	18.045	23.089
	10 mg L^{-1} Cd		15.429	0.978	0.019	0.370 ± 0.011		

[a] Determined by microwave digestion. [b] Derived from non-sorbing Br transport. [c] Calculated by area between input and sorption curves. [d] Optimizable parameters of nonequilibrium transport model. [e] Calculated by summing up Cu and Cd sorbed amounts in the same binary system. [f] Calculated by theoretically summing up Cu and Cd sorbed amounts in the corresponding single systems. [g] Not Applicable, because of the equivalence between nonequilibrium and equilibrium transport models.

soil pH was 7.6, measured at a 1:2 soil-to-water ratio. Measured by nitrogen gas adsorption (Micromeritics ASAP2010), the soil possessed a BET surface area of 7.04 m^2 g^{-1} and an unnoticeable micropore surface area. The cation-exchange capacity (CEC) of the soil was 34.9 meq/100 g, as determined by NH_4−Na exchange. The clay-size particles separated by the pipet method were determined with X-ray diffraction (XRD) analysis; the most abundant mineral was kaolinite. Total heavy-metal content in the soil was measured by X-ray fluorescence spectrometry (XRF). The soil contained 5.975% Fe, 24.987% Al, 3.068% Ca, and 0.355% Mn by mass.

Column Experiments. Eight columns of internal diameter 3.6 cm and length 10 cm were uniformly packed with the soil. The resulting bulk soil density and porosity were 1.508 g cm^{-3} and 0.433, respectively. The soil columns were slowly saturated with an upward-flowing background electrolyte of 0.03 M $NaNO_3$ (pH 5.5) from the bottom, and water saturation was gravimetrically checked. The experiments were conducted at 10 °C. A stable effluent pH and ionic strength was maintained after flushing with ~100 pore volumes. In addition, effluent concentrations of Fe, Al, Ca, and dissolved organic carbon indicated negligible dissolution of mineral oxides or soil organic matter during the breakthrough of Cu and Cd.

A pulse of Br solution (10 mg L^{-1} NaBr) was introduced into the columns. Preliminary study confirmed that Br did not sorb onto the soil. Effluent Br concentrations were analyzed by ion chromatography (IC) (Dionex DX-500). Four single-metal solutions and four binary-metal solutions of 10 or 100 mg L^{-1} Cu and/ or Cd (Table 1) were prepared by dissolving $Cu(NO_3)_2$ and/or $Cd(NO_3)_2$ in the background electrolyte of 0.03 M $NaNO_3$ adjusted to pH 5.5 by dilute HNO_3. These Cu and/or Cd concentrations could result in soil contamination ranging from tens to a thousand milligrams per kilogram of each metal, which covers the range usually encountered at sites. This slightly acidic condition is prevalent in regions with high annual rainfall and industrial sites. It was reported that no precipitation of Cu and Cd would occur until pH > 6−6.5 (16, 17). Influent solution was injected into the soil columns at an average pore-water velocity of 18.307 cm h^{-1}, simulating a forced-gradient condition of site remediation. The Cu and/or Cd solutions were injected into the soil columns. Effluent concentrations were measured by atomic absorption spectrometry (AAS) (Hitachi Z-8200). At the breakthrough plateau of both metals, soils were extruded for sequential extraction.

The breakthrough curves (BTCs) constructed by plotting relative concentration (effluent concentration/influent concentration) versus dimensionless time (pore volume) were analyzed with equilibrium/nonequilibrium transport equations using the optimization program CXTFIT version 2.1 (*18*). The transport model equations and data analysis had been described in the previous study (*19*). The Br BTCs (not shown) exhibited a symmetrical and sharp breakthrough that was well described by the equilibrium transport model, suggesting the absence of an immobile water region. Thus, a chemical (two-site) nonequilibrium model derived from rate-limited sorption was used to evaluate potential the nonequilibrium transport behavior of Cu and Cd. The Br BTCs were modeled with an equilibrium transport equation involving optimization of the dispersion coefficient D, which was assumed to be the same for Cu and Cd transport in the same column. The retardation factor R of heavy-metal transport was calculated by the area between the step input curve and the sorption BTCs (*20*). Thus, the simulation of the equilibrium model contained a zero fitting parameter; while that of the nonequilibrium model involved optimization of two parameters, F and α (fraction of instantaneous sorption and first-order rate coefficient (h^{-1}), respectively).

Batch Kinetics. The batch kinetics study was performed in polypropylene centrifuge tubes at solid concentrations of 20 g L^{-1} and 100 g L^{-1}, in order to illustrate the effect of metal-to-solid ratios on competition. All experiments were triplicated at 10 °C. Prior to heavy-metal sorption, the soil was equilibrated with the background solution of 0.03 M $NaNO_3$ (pH 5.5) three times for 24 h each. Single and binary solutions consisted of 10 or 100 mg L^{-1} Cu and/or Cd in background electrolyte. The tubes containing soil suspension were tumbled at 25 rpm for a total of 14 reaction times ranging from 1 min to 7 days; then they were centrifuged at 3500 rpm for 10 min. The Cu and Cd concentrations in the supernatant were measured by AAS, and the sorbed amounts were calculated by subtraction. The soil samples were analyzed with sequential extraction.

Sequential Extraction. The soil samples of batch kinetics and column experiments were pre-washed and freeze-dried. The extractions, based on the procedures mentioned in the literature (*9*, *21*, *22*) with a minor modification (Table S1, Supporting Information), were carried out progressively on 1 ± 0.005 g of the soil samples in 30-mL centrifugation tubes (except the final step of microwave digestion) to minimize soil loss. Following each extraction, the samples were centrifuged at 3500 rpm for 10 min at room temperature, and the concentrations of Cu and Cd in the supernatant of were analyzed using AAS. The samples were then washed with 10 mL of deionized water prior to the next extraction

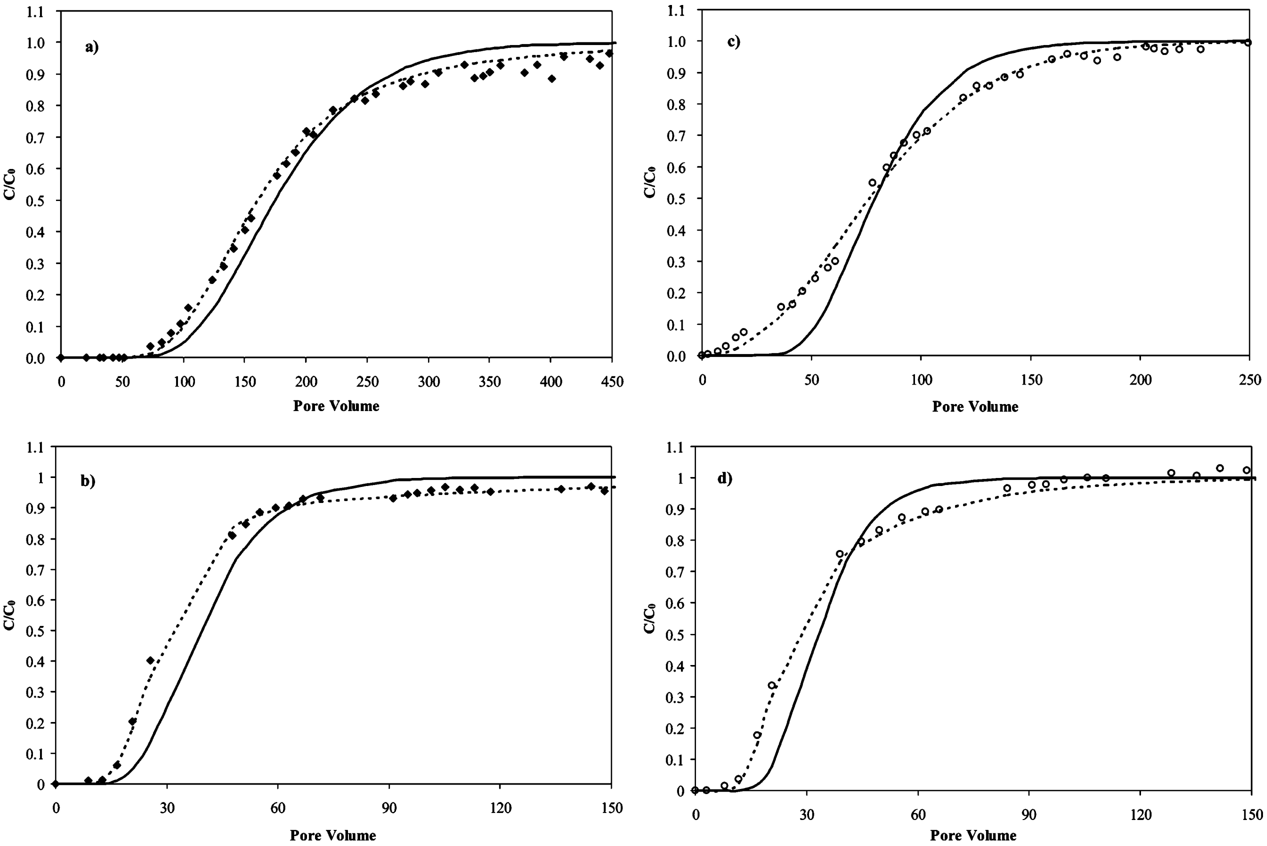

FIGURE 1. Experimental data and optimized simulations for Cu or Cd transport in the soil: (a) 10 mg L^{-1} Cu; (b) 100 mg L^{-1} Cu; (c) 10 mg L^{-1} Cd; (d) 100 mg L^{-1} Cd (◆ Cu; ○ Cd; — equilibrium transport model; ----- nonequilibrium transport model). Effluent pH values dropped from 5.5 ± 0.1 to 4.7–5.3 during the course of heavy metal transport suggesting proton release by metal sorption.

step. No visible residues were left after the final step of sequential extraction. The extraction experiments were triplicated. The sum of heavy-metal contents of the five extractions was compared with the total heavy-metal contents in soil determined by total acid digestion in a microwave oven. For soil samples from column experiments, Cu recovery was 96–106% and Cd recovery was 93–102%; for soil samples from batch kinetics, Cu recovery was 87–108% and Cd recovery was 85–101%. An acceptable accuracy of this sequential extraction scheme was therefore indicated.

Results and Discussion

Competitive Heavy-Metal Transport in Soil. Figure 1 displays the transport of Cu and Cd alone in the soil columns using influent concentrations of 10 and 100 mg L^{-1}. From the breakthrough curves (BTCs), Cu was more strongly sorbed and retarded during transport than Cd, which is in line with the selectivity sequence obtained from past batch studies (*7, 8*). Besides, the heavy-metal transport at low input concentration was more retarded, indicating a heterogeneous nature of sorption which leads to stronger affinity for metal cations at lower concentration. Asymmetric Cu and Cd BTCs were better described by a nonequilibrium transport model. The observed nonequilibrium transport behavior probably results from rate-limited sorption.

The binary Cu and Cd transport behaviors in the soil under various metal loadings are shown in Figure 2. Competition significantly reduced the retardation of Cd transport but marginally affected Cu transport, as reflected by comparing retardation factors of single- and binary-metal system (Table 1). This is expected from their corresponding sorption strength in the single-metal system and agrees with previous findings (*4, 5*). However, the extent of competition depends on metal loadings. The total amounts of Cu and Cd retained (mmol kg^{-1}) in the binary-metal system were smaller than the sum of the amounts of Cu and Cd that can be sorbed alone (Table 1), indicating that competition exists and some sorption sites are common for both Cu and Cd sorption. The difference was larger, standing for a more significant competition, at higher metal concentrations. The ratio of metal loading to sorption site density was also found important in other studies (*23, 24*). Under the column conditions of this study shown in Table 1, all metal loadings in the binary-metal system (>11 mmol kg^{-1}) appear to be sufficiently high that the competitive effect constantly existed and increased with metal loadings.

For Cu and Cd competitive transport (Figure 2), the effluent concentrations of Cd exceeded the respective influent concentrations by 10% following the initial breakthrough fronts, before reaching a plateau of the influent levels. This overshooting phenomenon of Cd appears to arise from the competitive sorption of Cu (*25*). The relatively weakly sorbing Cd migrated ahead of Cu due to a much smaller retardation, and therefore, initially sorbed on the soil in the absence of Cu competition (*26*). However, part of the sorbed Cd was then remobilized due to its displacement by the subsequent breakthrough of Cu, leading to normalized effluent concentrations greater than unity. Interestingly, modeling the competitive transport behavior demonstrated that Cd transport, except the overshooting portion, could be described by an equilibrium model simulation. Equilibrium Cd transport was corroborated by an indistinguishable nonequilibrium model simulation and corresponding estimated parameter values (Table 1). Conversely, Cu transport still illustrated nonequilibrium transport behavior that the deviation between Cu BTCs and equilibrium model simulation was even greater in the presence of competition. The contrasting Cd and Cu transport behaviors under competition cannot be

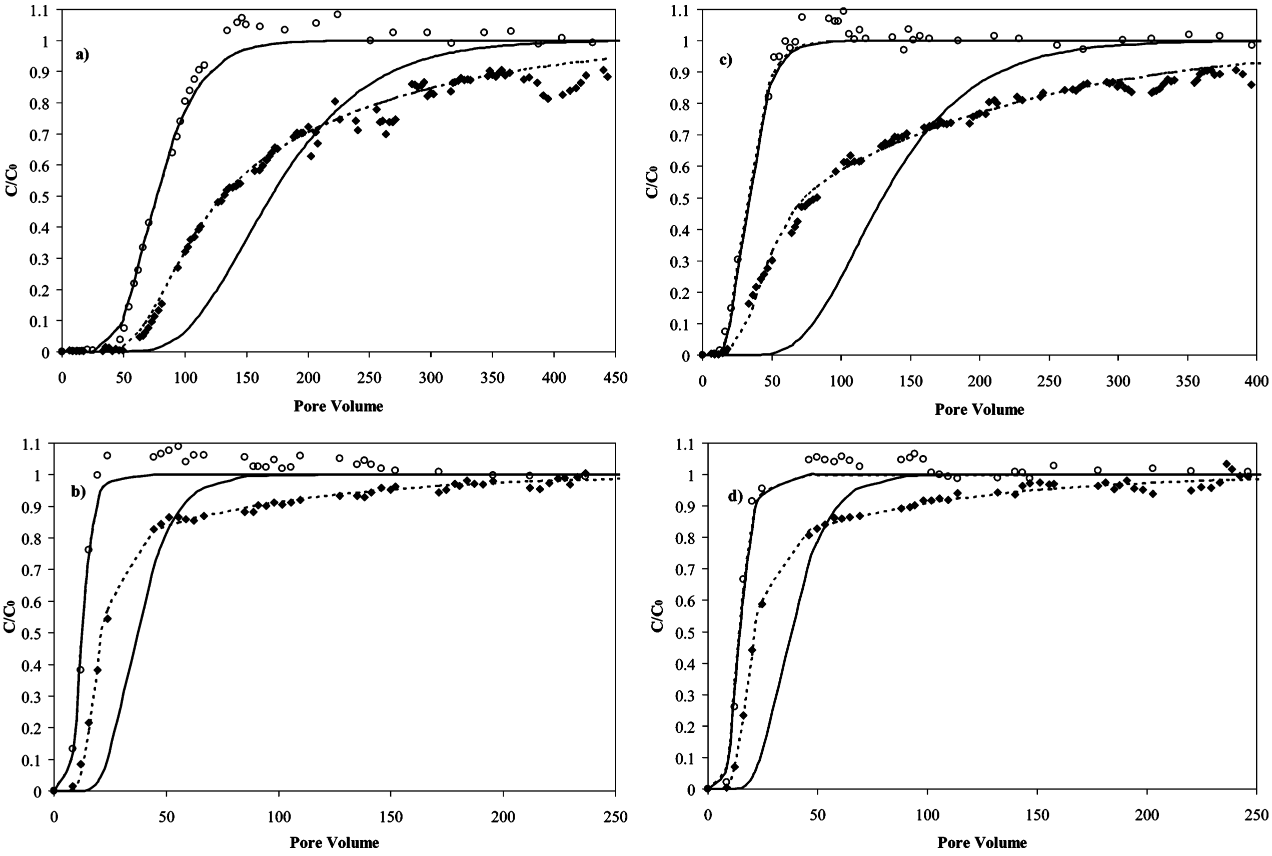

FIGURE 2. Experimental data and optimized simulations for competitive Cu and Cd transport in the soil: (a) 10 mg L^{-1} Cu and 10 mg L^{-1} Cd; (b) 100 mg L^{-1} Cu and 100 mg L^{-1} Cd; (c) 10 mg L^{-1} Cu and 100 mg L^{-1} Cd; (d) 100 mg L^{-1} Cu and 10 mg L^{-1} Cd (◆ Cu; ○ Cd; — equilibrium transport model; ----- nonequilibrium transport model).

explained solely by modeling the transport data that lead to the following evaluation of the competitive effect on sorption kinetics and fractionation.

Batch Sorption Kinetics. Competition reduced the amount of sorption, of which Cu was less affected than Cd (Figure S1, Supporting Information). However, the competitive effect was not observed in systems containing 10 mg L^{-1} Cu and 10 mg L^{-1} Cd at a soil-to-solution ratio of 1:10, that is, the sorption amount and kinetics were virtually identical (not shown). An excess of surface sites for metal cations negated competition, explaining why the competitive effect was not necessarily observed at low heavy-metal concentrations (*24, 27, 28*). The competitive effect exhibited in all column experiments was probably because the flowing solution continuously supplies metal cations to the soil, which is different from a batch system.

Similar values of rate coefficients were obtained by fitting the kinetic data of single- and binary-metal systems with an empirical power function ($r^2 > 0.91$), which agrees with the previous findings (*10*) and indicates that competition did not apparently affect the sorption rate. However, while the apparent equilibrium time was about 4 days for Cu irrespective of the presence of Cd, the apparent equilibrium time of Cd sorption was curtailed from about 1 day to 30 min when Cu was present and competed for sorption sites (Figure S1, parts c and d, Supporting Information). It appears that Cu competition reduced the instantaneous Cd sorption while eliminating the rate-limited Cd sorption, which was probable if the latter was of limited capacity and out-competed by Cu.

Sequential Extraction. The competitive effect on nonspecific and specific sorption was then evaluated with sequential extraction, of which the five fractions from exchangeable to residual (Table S1, Supporting Information) are operationally defined. In terms of increasing metal binding strength, sorption on the first two fractions is weak and regarded as nonspecific, while sorption on the latter three fractions is of high binding strength and considered specific. Figure 3 presents the results for soil samples of batch kinetics. In general, metal cations were spontaneously sorbed on exchangeable and carbonate fractions, of which ~90% were completed in 1 min and equilibrium was attained within 30 min. But since sorption on other three fractions continued with time, the distribution percentage of these two fractions decreased after 30 min. For Cu and Cd sorption in a single-metal system (Figure 3, parts a,b and e,f), sorption on the latter three fractions required a much longer reaction time (about 7 days) to reach equilibrium. Thus, specific sorption of Cu and Cd was rate-limited. The smaller metal percentages of the oxide, organic matter, and residual fractions at higher metal concentrations indicated that their sorption capacity was more limited than exchangeable and carbonate fractions.

Although Cu sorption was reduced by Cd competition to some extent in batch experiments, its distribution among fractions was nearly unaffected (Figure 3, parts a,c and c,d). By contrast, Cd distribution was noticeably changed (Figure 3 parts e and g, and parts f and h). The total amount of nonspecific and specific sorption of Cd was suppressed by strongly sorbing Cu. The percentage of nonspecific sorption of Cd was found higher because it was relatively less reduced than other fractions. On the other hand, although specific sorption of Cd was slightly inhibited on the oxide fraction and unaltered on the residual fraction, it was almost eliminated on the organic matter fraction. Since these strong binding sites were of limited capacity, a relatively small concentration of a strongly competing Cu might occupy all these sites (*29*). As specific sorption was shown to be rate-limited, its sharp reduction on the organic matter fraction

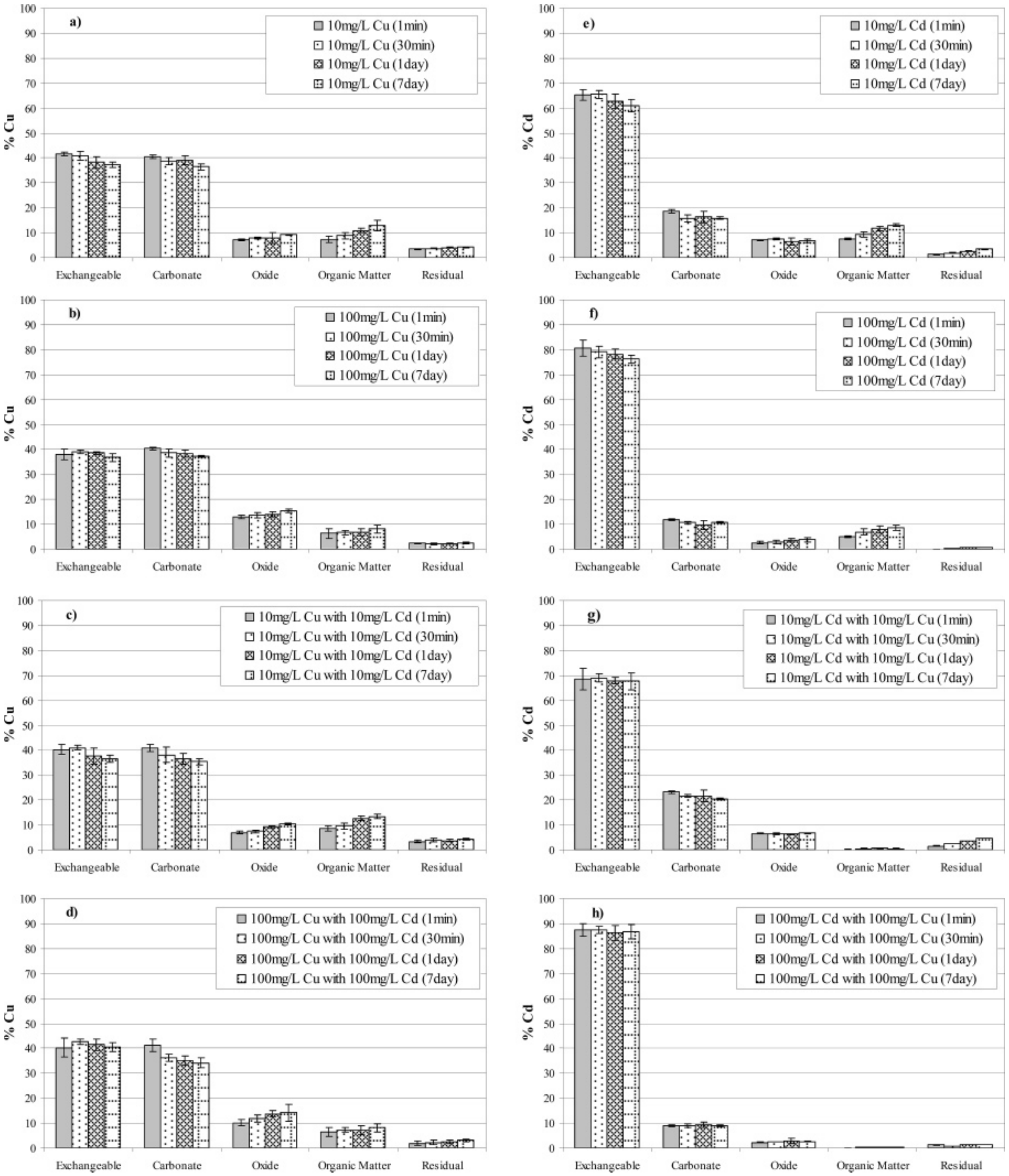

FIGURE 3. Distribution of Cu and Cd in soil samples of the batch kinetics experiment after four reaction durations (1 min, 30 min, 1 day, and 7 days): (a,b) 10 mg L^{-1} and 100 mg L^{-1} Cu alone; (c,d) 10 mg L^{-1} and 100 mg L^{-1} Cu in the presence of Cd of equal concentration; (e,f) 10 mg L^{-1} and 100 mg L^{-1} Cd alone; (g,h) 10 mg L^{-1} and 100 mg L^{-1} Cd in the presence of Cu of equal concentration. The results are the average of triplicates, and error bars represent standard deviation.

seems to account for the shorter equilibrium time observed in batch kinetics.

The sequential extraction results of the soil extruded from column experiments are illustrated in Figure 4. The major reduction of Cu sorption due to Cd competition occurred in exchangeable and carbonate fractions; sorption on oxide, organic matter, and residual fractions was marginally hindered. Therefore, the relative contribution of rate-limited specific sorption was greater and resulted in more significant nonequilibrium transport behavior as observed in column experiments. On the contrary, Cd sorption on all fractions except residual was clearly suppressed by Cu competition. The rate-limited specific sorption of Cd was brought to a minimal amount, accounting for the observed equilibrium transport behavior in column study.

It can be remarked upon the above results that nonspecific sorption (exchangeable and carbonate fractions) was subject to competition for both Cu and Cd depending on their relative concentrations. Part of the specific sorption (residual fraction) was unique for a particular metal and indifferent to competition. However, the rest of the specific sorption (oxide and organic matter fractions) of Cd was strongly prone to competition while that of Cu was slightly affected. This was probably due to different sorption characteristics and preference of soil components, which can be elucidated with the aid of spectroscopic studies reported by other researchers.

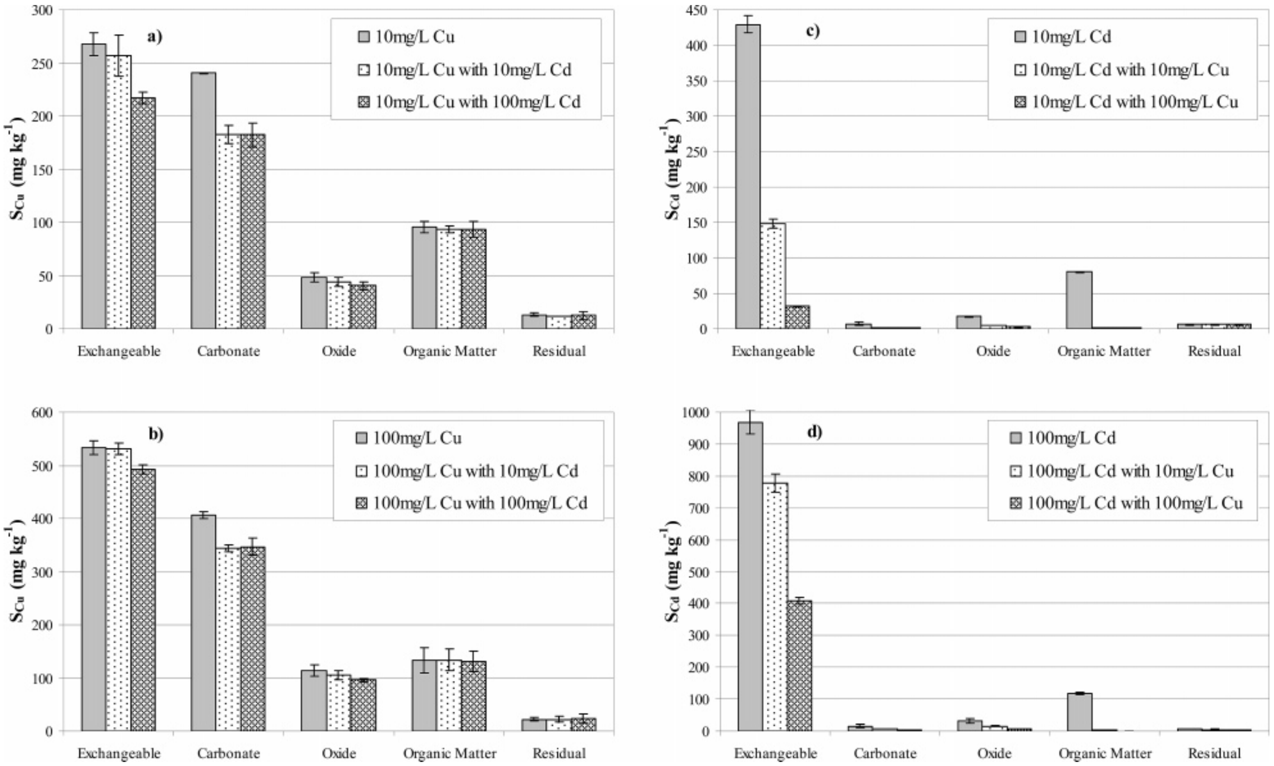

FIGURE 4. Distribution of sorbed Cu and Cd in the soil after heavy-metal breakthrough in column experiments using various heavy-metal loadings: (a,b) 10 mg L^{-1} and 100 mg L^{-1} Cu in the presence/absence of Cd; (c,d) 10 mg L^{-1} and 100 mg L^{-1} Cd in the presence/absence of Cu. The results are the average of triplicates, and error bars represent standard deviation.

Since surface precipitation of Cd is unlikely due to its large ionic radius (*25*) and that of Cu occurs at pH values above 6 (*30*), inner-sphere complexation on soil organic matter functional groups and oxide or clay mineral surfaces appears to be responsible for specific sorption which can be subject to competition. Although the chemical reaction of inner-sphere complexation may take place in milliseconds, slow sorption was often observed and attributed to micropore or surface diffusion toward high-energy sites (*25*, *27*). Of inner-sphere complexation on Fe oxide minerals, XAFS results indicated that Cu binds as bidentate, edge-sharing complexes (*11*), whereas Cd sorbs as bidentate, corner- or edge-sharing complexes depending on types of minerals (*31*). Thus, some sorption sites on Fe oxides might be competed for by Cu and Cd. In addition, spectroscopic studies also confirmed the formation of inner-sphere surface complexes of Cu and Cd with soil humic substances in the pH range of 4 to 7 (*17*, *32*−*34*). At the metal loadings of this study, it is likely that both Cu and Cd form complexes predominantly with O-containing functional groups, at which Cu is preferentially sorbed over Cd according to the Misono softness parameter (*35*). Therefore, a strong competition effect was observed for Cd sorbed on an organic matter fraction.

In addition to the chemical properties of cations which determine the selectivity and sorption affinity, the types of bonding and the characteristics of surface sites are crucial to the competitive effect. The Cu competition on rate-limited specific sorption of Cd, particularly on organic matter, is probably accountable for the observed change of Cd transport behavior from nonequilibrium to equilibrium. Further verification can be facilitated by a combination of spectroscopic studies and column experiments in the future. In view of engineering implications of these findings, Cd may impose a greater extent of contamination under Cu competition due to a dramatic reduction of sorption and equilibrium transport behavior, while Cu may take a longer time to be released from soils due to the persistent presence of rate-limited specific sorption and nonequilibrium transport behavior.

Supporting Information Available

Sequential extraction scheme and batch sorption kinetics of Cu and Cd in the presence and absence of competition. This material is available free of charge via the Internet at http://pubs.acs.org.

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