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# Immobilization of Zinc and Cadmium by Montmorillonite Compounds: Effects of Aging and Subsequent Acidification

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The addition of aluminum treated montmorillonites as binding agents that immobilize heavy metals is an innovative approach for the remediation of arable soils polluted with heavy metals. We investigated the influence of aging and subsequent sudden acidification on the binding of zinc and cadmium by montmorillonite, Al-montmorillonite and Al<sub>13</sub>-montmorillonite. The addition of HCl led to a drop in pH and a partial remobilization of the sorbed heavy metals. Al-montmorillonite and Al<sub>13</sub>-montmorillonite exhibited a higher pH buffer capacity than montmorillonite. With increasing aging, sorption of zinc on Al-montmorillonite and Al<sub>13</sub>-montmorillonite increased, probably due to a partial incorporation in the aluminum hydroxide lattice. Sorption and desorption were hysteretic with respect to pH, i.e., desorption required lower pH values than adsorption to reach the same state of metal partitioning between solid phase and solution. In addition, these minerals enhance the pH buffer capacity of the soil. The results suggest that Al-montmorillonite and Al<sub>13</sub>-montmorillonite are suitable minerals to be used as binding agents for the gentle immobilization of heavy metals in polluted soils.

## Introduction

Application of metal containing pesticides, commercial fertilizers, and sewage sludge as well as air-borne pollution has led to widespread accumulation of heavy metals in agricultural soils. High concentrations of heavy metals in soils threaten soil fertility, ecosystem functions, and human health. For extensive areas of contaminated agricultural land, remediation techniques, which reduce toxicological risks without compromising soil fertility, are in demand.

Definitive soil remediation requires the extraction of the polluting metals. Unfortunately, remediation techniques available to date, e.g., soil washing, are rather expensive as well as destructive to soil fertility, while gentle extraction techniques such as phytoremediation are still not operational on a large scale (1–3). Immobilization could provide a quick solution to reduce the risks caused by high concentrations of heavy metals, at least temporarily until better solutions are available. For soils contaminated by heavy metals, liming is an often-proposed method to increase the pH and to reduce the solubility of heavy metals (4–6). However, an increase

in pH due to liming may also cause negative effects, such as reduced manganese and phosphate availability to plants (7, 8), changes in biocenoses in soils, and increased nitrate concentrations in drainage water or humus decomposition followed by a mobilization of copper and lead (9). Other immobilization methods are based on binding agents which work more or less specifically, e.g., cation exchangers (10), zeolites (6, 11), organic materials (7, 12), iron and manganese oxides (13), brown coal (14), or clay minerals (15, 16). The presence of these binding agents may decrease dissolved heavy metal concentrations. Again, negative effects, such as immobilization of nutrients, may also occur. Furthermore, organic substances are subject to decomposition, while iron and manganese oxides may be dissolved under reductive conditions.

Furrer et al. (17) proposed the use of montmorillonites modified by aluminum as binding agents. These compounds show a preferential sorption of heavy metals compared to other bivalent cations. In a previous paper (18) it was reported that Al-montmorillonite and Al<sub>13</sub>-montmorillonite immobilized nickel, copper, zinc, and cadmium, whereas the effect on the dissolved lead concentrations was rather small. Nickel, copper, and zinc were sorbed specifically on Al-montmorillonite and Al<sub>13</sub>-montmorillonite. The sorption of zinc and nickel increased with time, probably due to structural rearrangement in the aluminum interlayer (18). Al-montmorillonite was effective in the pH range 6–8 for nickel and zinc, in the pH range 4–6 for copper, and in the pH range 7–9 for cadmium (18). The addition of montmorillonite and Al-montmorillonite in pot experiments to a neutral soil resulted in the immobilization and reduction of the plant available heavy metals without inducing nutrient deficiency in red clover (19).

In the experiments reported here, we studied the influence of sudden acidification on freshly prepared as well as on aged suspensions containing binding agents and heavy metals.

## Experimental Section

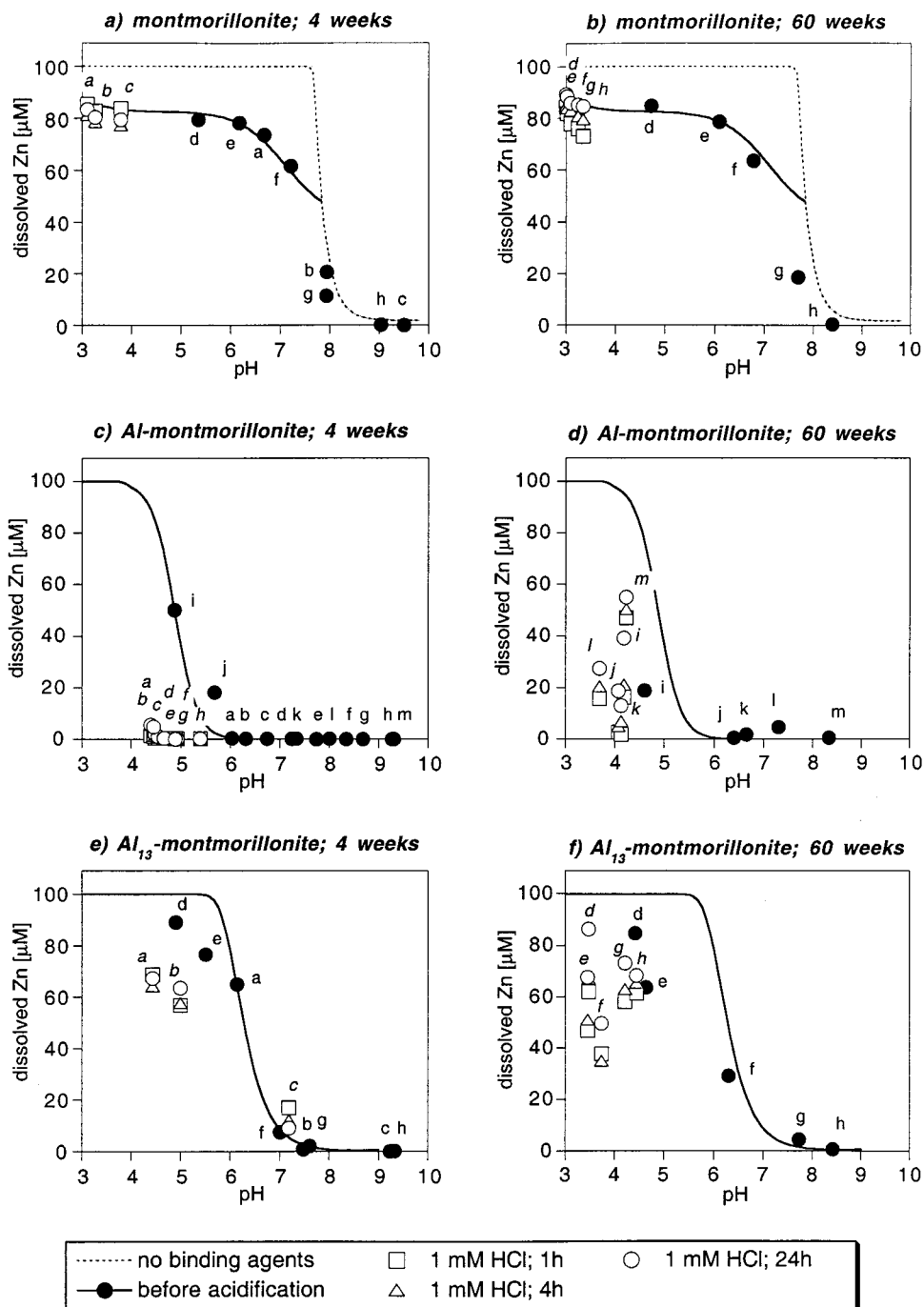
**Materials.** Montmorillonite originating from Crook County, WY (SWy-1, Clay Minerals Society) was used. The particle fraction  $\leq 2 \mu\text{m}$  (Stokes' diameter) was separated by sedimentation technique. The sodium form was obtained by washing the clay fraction three times with 1 M NaCl followed by four washings with Nanopure water. The stock suspension contained 15 g montmorillonite/L and was stored in the dark.

Al<sub>13</sub>-montmorillonite was prepared as described by ref 18. Al<sub>13</sub> solution was added to the montmorillonite stock suspension until a ratio of 2 mmol of Al(III)/(g of clay) was reached. Al-montmorillonite was prepared by the addition of AlCl<sub>3</sub> solution to the montmorillonite stock suspension, until again a ratio of 2 mmol of Al(III)/(g of clay) was reached. The suspension was slowly titrated with 0.1 M NaOH to an OH/Al ratio of 2.45 (18). Al<sub>13</sub>-montmorillonite as well as Al-montmorillonite suspensions were washed three times with Nanopure water and used for the experiments within 1 week. All data on weight are referred to untreated montmorillonite although the presence of aluminum increased the weight of Al-montmorillonite by 15% and of Al<sub>13</sub>-montmorillonite by 17%. All chemicals were reagent grade.

**Methods.** In a first step, a total of 64 batch experiments has been prepared in the pH range 4–10 to quantify the sorption of zinc and cadmium on the binding agents. Batch experiments were performed in glass vessels and with a suspension volume of 100 mL. Water, NaClO<sub>4</sub>, montmoril-

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**FIGURE 1.** Fate of zinc in the presence of binding agents after addition of 1 mmol of HCl/L, after 4 and 60 weeks aging: (a, b) montmorillonite; (c, d) Al-montmorillonite; (e, f)  $Al_{13}$ -montmorillonite. The experimental points have been labeled to show the influence of acidification on the individual batch experiments.

lonite (untreated or previously treated with  $Al_{13}$  or Al), chloride salts of heavy metals, and HCl or NaOH were added to achieve a final montmorillonite concentration of 2 g/L, an ionic strength of 0.1, and zinc or cadmium concentrations of 100  $\mu$ M. The batch vessels were purged with argon to reduce  $CO_2$  partial pressure, closed tightly, and shaken at 200 rpm at room temperature during 4 weeks. The pH was measured under argon several times and, if necessary, adjusted with HCl or NaOH. A total of 28 batch vessels were left to age for 4 weeks ("fresh suspensions") and 36 batch vessels for 60 weeks ("aged suspensions"). Then, pH was measured, and 10 mL of the suspensions was taken and centrifuged at 5000 rpm (3990g) for 30 min. The supernatants were filtered (cellulose nitrate, 0.05  $\mu$ m) and acidified, and the concentrations of heavy metals in the filtrates were analyzed by ICP-

AES for dissolved concentrations of silicon, aluminum, magnesium, and heavy metals.

In a second step, the influence of acidification has been quantified by the addition of 90  $\mu$ L of 1 M HCl solution to the remaining 90 mL of solution in each batch vessel. These suspensions containing 1 mM HCl were shaken, and samples were taken after 1, 4, and 24 h. One day after the first acidification, 1 mM NaOH was added to six batch vessels to assess the influence of a short-term acidification on dissolved heavy metal concentrations. The others were treated with HCl to investigate the influence of dissolution of the binding agents on heavy metal remobilization. For this purpose, HCl was added after 48 h until a total concentration of 11 mM HCl was reached. Again, samples were analyzed for dissolved silicon, aluminum, magnesium, and heavy metals.

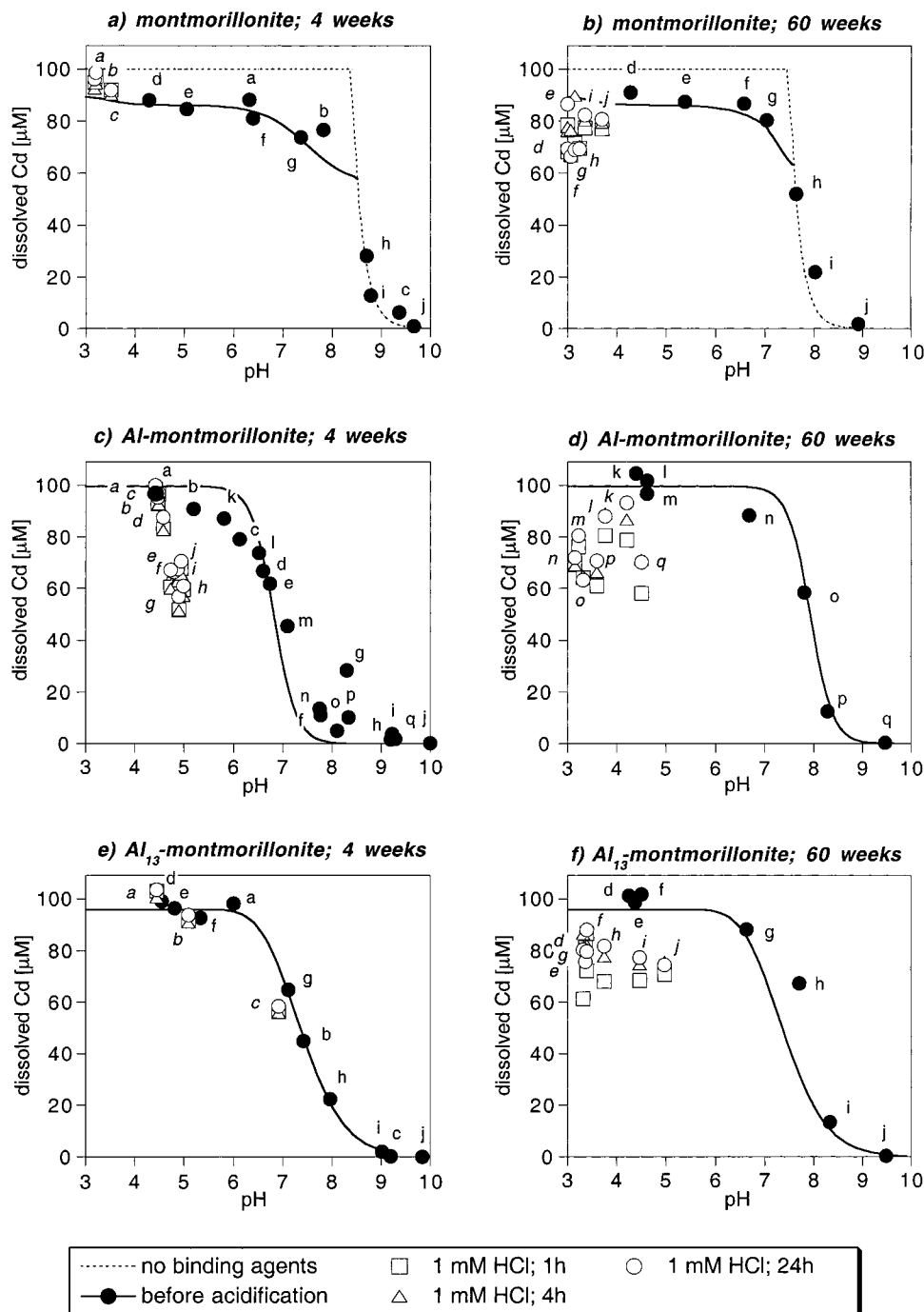


FIGURE 2. Fate of cadmium in the presence of binding agents after addition of 1 mmol of HCl/L, after 4 and 60 weeks aging: (a, b) montmorillonite; (c, d) Al-montmorillonite; (e, f) Al<sub>13</sub>-montmorillonite. The experimental points have been labeled to show the influence of acidification on the individual batch experiments.

The pH measurements were carried out with a combined pH electrode (Metrohm 6.0204.100) connected to a digital voltmeter (Metrohm 713). This equipment was calibrated prior to the measurements by acid–base titration in the respective ionic media. The dissolved concentrations of zinc and cadmium in the presence of the solid phases ZnO and CdCO<sub>3</sub> were calculated using the program MICROQL (20) with thermodynamic constants from refs 21 and 22, corrected for ionic strength using the Davies equation. Formation of a solid CdCO<sub>3</sub> phase was observed since the batch vessels were not completely gastight. The precipitation of CdCO<sub>3</sub> was slow. On the basis of the observed pH shift after 4 and 60 weeks, partial CO<sub>2</sub> pressures of  $9 \times 10^{-9}$  atm and  $6 \times 10^{-7}$  atm, respectively, were calculated.

## Results and Discussion

**Influence of Acidification on Heavy Metal Binding.** The solid circles in Figures 1 and 2 represent the concentrations of zinc and cadmium in the presence of the binding agents after aging times of 4 and 60 weeks. The solid lines represent the theoretical concentrations of these heavy metals calculated with the surface complexation model given in ref 18. While the adsorption of zinc on montmorillonite did not change with time (Figure 1a,b), a shift to lower pH is evident for cadmium (Figure 2a,b). This effect is due to ongoing precipitation of CdCO<sub>3</sub> and not to kinetically limited adsorption.

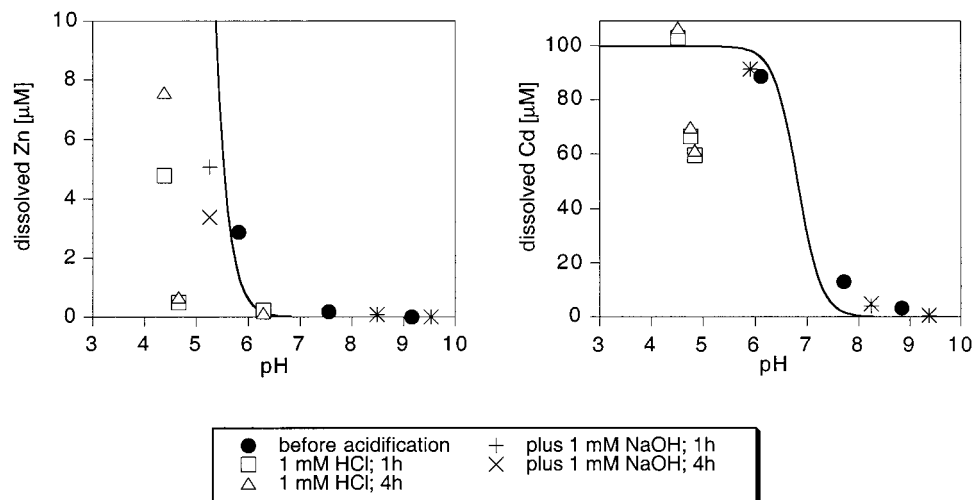


FIGURE 3. Remobilization and readsorption of zinc and cadmium in the presence of Al-montmorillonite before and after the addition of 1 mM HCl and the subsequent addition of 1 mM NaOH. The solid lines represent the calculated zinc and cadmium concentrations in the presence of Al-montmorillonite after 4 weeks equilibration time. Note that the scale for zinc concentration is from 0 to 10  $\mu\text{M}$ . The experimental points have been labeled to show the influence of acidification on the individual batch experiments.

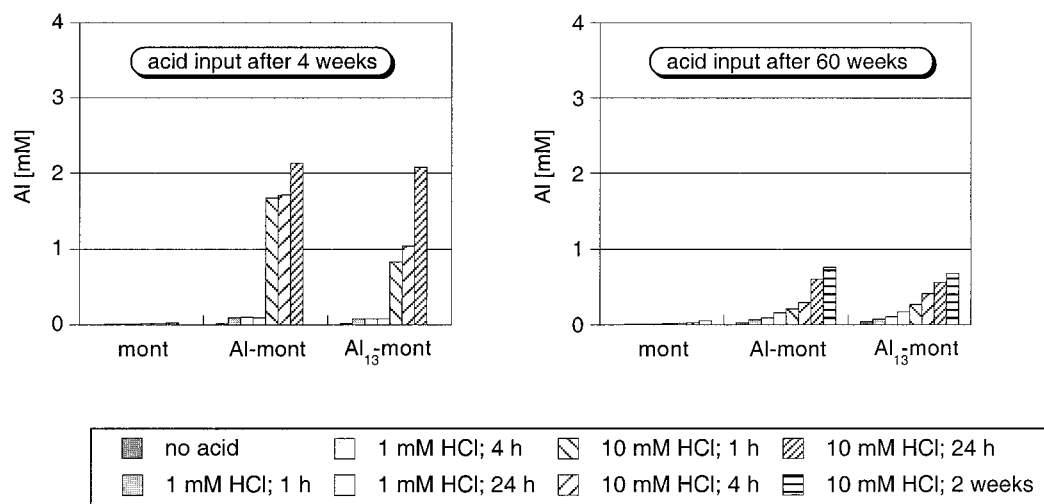


FIGURE 4. Dissolution of aluminum after the input of 1 and 10 mmol of HCl/L to suspensions containing 2 g of montmorillonite/L (untreated or previously treated with 4 mM Al or  $\text{Al}_{13}$ ).

The open symbols in Figures 1 and 2 represent the cadmium and zinc concentrations after the addition of 1 mM HCl. The addition of 1 mM HCl decreased pH to approximately 3 and increased the dissolved zinc and cadmium concentrations in the presence of montmorillonite to approximately 80  $\mu\text{M}$  (Figures 1a,b and 2a,b). The remaining sorption of heavy metals on montmorillonite under neutral and acidic conditions is mainly due to ion exchange reactions on the permanently negatively charged ion exchange sites of the montmorillonite, while edge site complexation is not important in this pH range (18, 23, 24). Thus, a shift in pH from 7 to 3 has little influence on the sorption equilibria of cadmium and zinc on the cation exchange sites of montmorillonite.

In contrast to adsorption on montmorillonite, zinc sorption on Al- and  $\text{Al}_{13}$ -montmorillonite increased with time. After 60 weeks of aging, the sorption of zinc to Al-montmorillonite and  $\text{Al}_{13}$ -montmorillonite has increased even further (Figure 1d,f) in comparison to 4 weeks aging (Figure 1c,e). For cadmium (Figure 2c–f) the sorption edge was shifted to higher pH values with time. Lothenbach et al. (18) concluded from X-ray and adsorption measurements that within half a year the interlayer Al- and  $\text{Al}_{13}$ -montmorillonite underwent structural rearrangements. During this rear-

rangement the zinc cations became incorporated into the aluminum hydroxide layer. No such incorporation was observed for the larger cadmium cations due to steric reasons (18). Similarly, the structural incorporation of Mn, Ni, Cu, and Zn during the aging of hydrous iron oxides was observed, while for the larger Pb and Cd cations only minimal incorporation is reported (25, 26). Scheidegger et al. (27) confirmed with XAFS analysis the formation of mixed nickel–aluminum hydroxides on pyrophyllite.

In the presence of fresh Al-montmorillonite, the addition of 1 mM HCl and the subsequent pH decrease moved the observed sorption edge for both zinc (Figure 1c) and cadmium (Figure 2c) to lower pH values. In both cases, the sorption and desorption of heavy metals on fresh Al-montmorillonite were hysteretic with respect to pH; i.e., desorption (open symbols) occurred at lower pH values than the corresponding adsorption (closed symbols) after the addition of acid. A similar hysteresis effect was also observed after the subsequent addition of an equivalent amount of base (Figure 3). After the subsequent addition of base, the zinc and cadmium sorption on Al-montmorillonite returned to the course before acidification. As only zinc may be incorporated in the aluminum hydroxide lattice, processes occurring at the

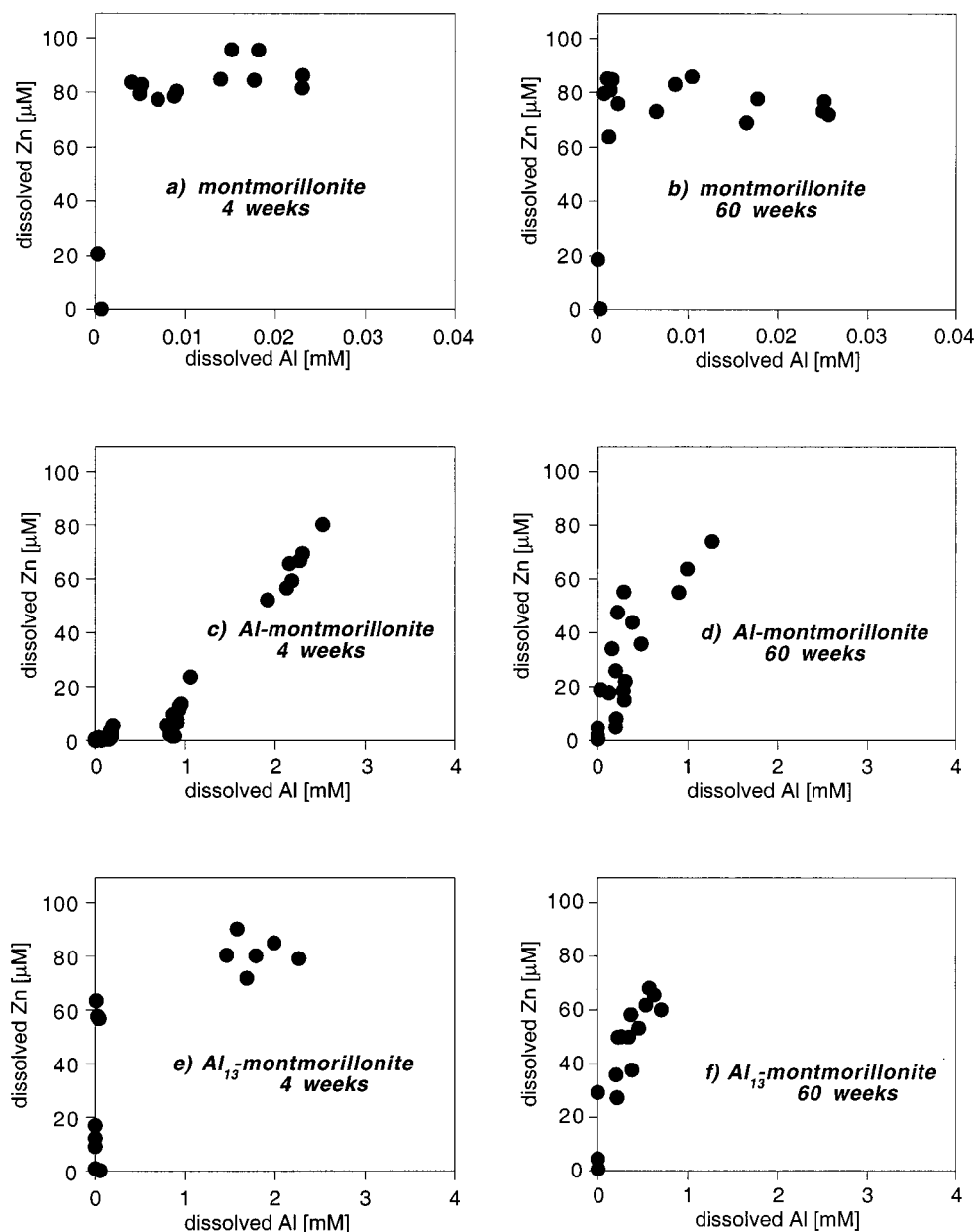


FIGURE 5. Dissolved zinc versus aluminum concentrations before and after the addition of 1 and 10 mM HCl to suspensions aged for 4 and 60 weeks. The suspensions contained 2 g of montmorillonite/L (untreated or previously treated with 4 mM Al or  $\text{Al}_{13}$ ) and 100  $\mu\text{M}$  zinc.

hydroxide surface, e.g. surface induced precipitation, must be responsible for this hysteresis phenomena.

Zinc sorption on fresh  $\text{Al}_{13}$ -montmorillonite showed a hysteresis effect similar to that on fresh Al-montmorillonite, although less distinct (Figure 1e), while cadmium sorption on fresh  $\text{Al}_{13}$ -montmorillonite did not show such an effect (Figure 2e). The addition of acid to suspensions of aged Al-montmorillonite and  $\text{Al}_{13}$ -montmorillonite resulted in a remobilization of most of the sorbed heavy metals (Figure 1d,f and 2d,f).

The observed hysteresis effects indicate a reduced sensitivity of metal immobilization to acidification as compared to nonhysteretic sorption. The addition of an equivalent amount of base (Figure 3) returned dissolved heavy metal concentrations to the state before acidification. This cycle may simulate a single event of acidification with subsequent neutralization. Such hysteresis effects indicate that the use of the described immobilizing agents may retard remobilization of heavy metals significantly in comparison to untreated soils.

**Buffer Capacity and Resistance to Dissolution of the Binding Agents.** The addition of 1 mM HCl shifts the pH in the montmorillonite suspensions close to pH 3; i.e., the pH buffer capacity of untreated montmorillonite is relatively small (Figure 1a,b). Al-montmorillonite and  $\text{Al}_{13}$ -montmorillonite exhibited a larger buffer capacity than montmorillonite (Figures 1 and 2). The addition of HCl to fresh Al-montmorillonite and  $\text{Al}_{13}$ -montmorillonite suspensions caused a less pronounced pH decrease than the addition of HCl to aged suspensions. After the addition of 1 mM HCl the pH values in the presence of fresh Al-montmorillonite converged around pH 5 (Figures 1c and 2c), i.e., in the pH range where protonation reactions involving  $\text{Al}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})^{2+}$ , and  $\text{Al}^{3+}$  occur (28). The surface hydroxyl groups of the Al-montmorillonite (4 mM aluminum) became protonated and buffered strongly. Dissolved aluminum concentrations did barely increase (Figure 4), indicating that the protonation of surface hydroxyl groups and not dissolution was responsible for pH buffering. Fresh  $\text{Al}_{13}$ -montmorillonite buffered as strongly as Al-montmorillonite (Figures 1e and 2e), although



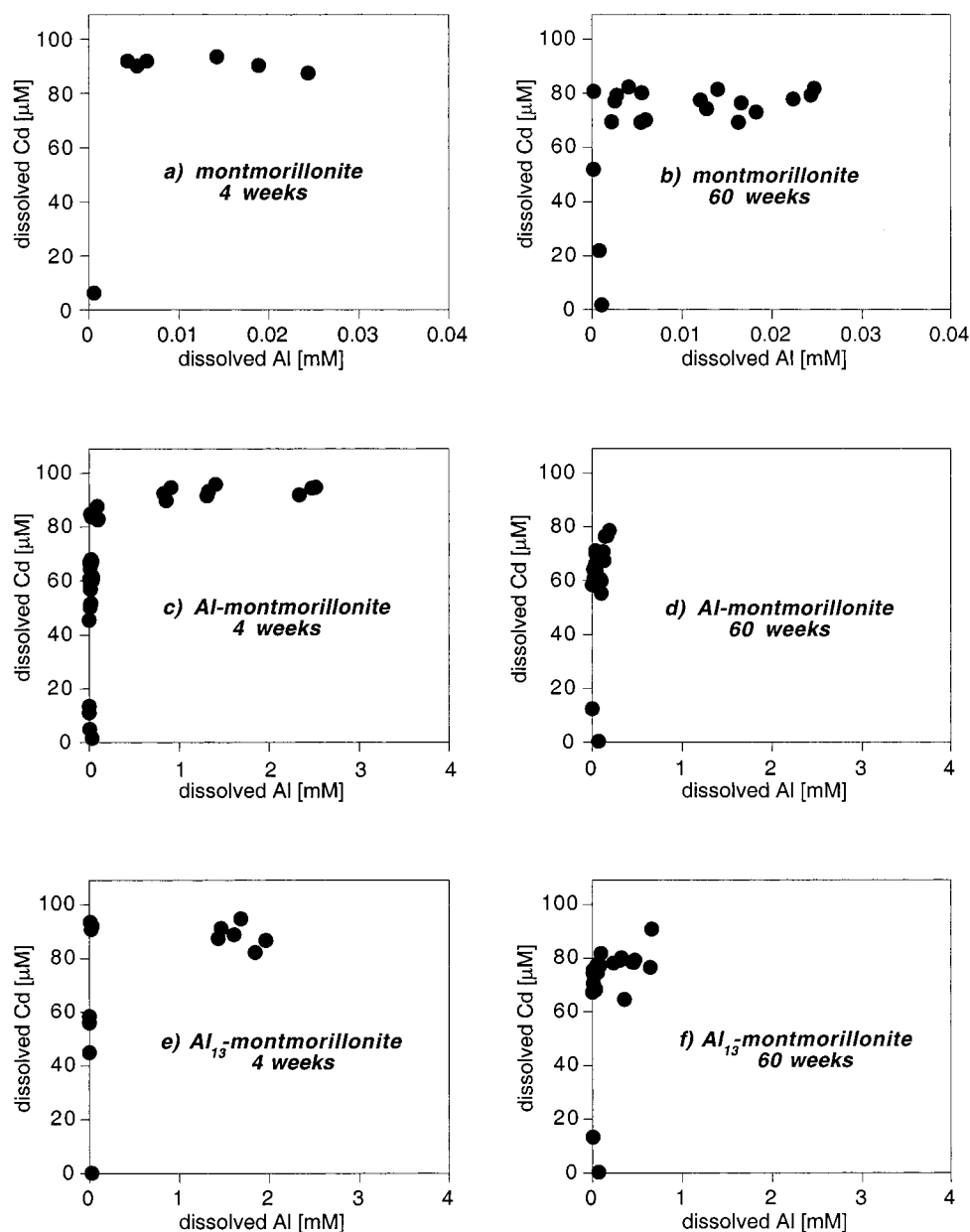


FIGURE 6. Dissolved cadmium versus aluminum concentrations before and after the addition of 1 and 10 mM HCl to suspensions aged for 4 and 60 weeks. The suspensions contained 2 g of montmorillonite/L (untreated or previously treated with 4 mM Al or  $\text{Al}_{13}$ ) and 100  $\mu\text{M}$  cadmium.

the resulting pH values were more spread out, indicating a more evenly distributed protonation of the hydroxide groups over the pH range. Similar to the observation in the presence of Al-montmorillonite, dissolved aluminum concentrations were barely increased after the input of 1 mM of HCl in the  $\text{Al}_{13}$ -montmorillonite suspensions (Figure 4). Aged Al-montmorillonite and  $\text{Al}_{13}$ -montmorillonite suspensions showed a smaller buffer capacity after the addition of 1 mM HCl (Figures 1d,f and 2d,f). This can be attributed to ripening processes that led to a more crystalline structure and therefore to a reduced number of surface hydroxyl groups.

The addition of 10 mM HCl to 4 weeks old Al-montmorillonite and  $\text{Al}_{13}$ -montmorillonite suspensions led within 24 h to the dissolution of approximately 50% of the aluminum added (Figure 4), whereas from the aged Al-montmorillonite and  $\text{Al}_{13}$ -montmorillonite only one-sixth of the total aluminum was dissolved. In view of the X-ray data of ref 18 the latter effect can be explained by rearrangement of aluminum hydroxides into more crystalline structures which exhibited slower dissolution kinetics.

**Dissolution of the Binding Agents and Remobilization of Heavy Metals.** A second input of 10 mM HCl to the suspensions decreased the pH to a value of approximately 2 and, as consequence, led to a slow dissolution of montmorillonite, Al-montmorillonite, and  $\text{Al}_{13}$ -montmorillonite (Figure 4) and to remobilization of zinc and cadmium. The ratios of dissolved aluminum to dissolved zinc (Figure 5) and cadmium (Figure 6) revealed some insights on heavy metal incorporation into the aluminum hydroxide lattice.

In the presence of montmorillonite, the addition of HCl resulted in dissolved zinc (Figure 5a,b) and cadmium (Figure 6a,b) concentrations between 80 and 90  $\mu\text{M}$  that were independent of the amount of aluminum dissolved by the progressive dissolution of montmorillonite (cf. Figure 4). No difference between the corresponding metal concentrations in fresh and aged montmorillonite suspensions could be detected. As zinc and cadmium sorb under acidic conditions predominately on ion exchange sites (18), also the lowering of pH to a value of 2 had little effect on the adsorption of these metals by montmorillonite.

Parts c and d of Figure 5 show a positive correlation between the amount of remobilized aluminum and dissolved zinc in the presence of Al-montmorillonite. This indicates that zinc is incorporated in the aluminum lattice and remobilized only after the dissolution of the aluminum hydroxide lattice. The slope near 1 between dissolved zinc and aluminum (Figure 5c) indicates a rather uniform distribution of the incorporated zinc in the relatively amorphous aluminum hydroxide layers of fresh Al-montmorillonite. In aged Al-montmorillonite, zinc was incorporated near the surface of the crystalline aluminum hydroxide lattice, as indicated by the preferential dissolution of zinc sorbed (Figure 5d). The formation of a crystalline aluminum lattice during aging led to an accumulation of zinc at the surface of the aluminum hydroxide structure. McBride (29) proposed that copper incorporated in aluminum oxide precipitates preferentially occupies positions at or near the oxide surface to avoid internal charge imbalances. Similarly, for Cd and Ni the formation of a solid solution in a surface film on calcite has been described (30, 31). In contrast to zinc, cadmium sorbed on fresh and aged Al-montmorillonite was remobilized before a substantial amount of aluminum was released into solution (Figure 6c,d). This preferential release indicates that cadmium was sorbed on surface sites of the aluminum hydroxide lattice and that no or only little incorporation occurred. This confirms the observation of Ford et al. (25) and Martinez and McBride (26) who observed structural incorporation of Mn, Ni, Cu, and Zn during the aging of hydrous iron oxides, but not for the larger Pb and Cd cations.

Zinc sorbed on fresh Al<sub>13</sub>-montmorillonite (Figure 5e) was readily desorbed after the addition of acid to the suspensions. In fresh Al<sub>13</sub>-montmorillonite, the Al<sub>13</sub>-polymers are evenly distributed in the interlayer space of the montmorillonite and the cations sorb specifically on the surface sites of these Al<sub>13</sub>-polymers (18) where they were readily be remobilized by the addition of acid (Figure 5e). In contrast, the desorption of zinc from aged Al<sub>13</sub>-montmorillonites showed a positive linear correlation with aluminum in solution (Figure 5f). During aging, the interlayer Al<sub>13</sub> converted to solid Al(OH)<sub>3</sub>, where zinc is probably incorporated and occupies positions near the surface of the aluminum hydroxide. In the case of cadmium, more than 80% of cadmium sorbed on fresh or aged Al<sub>13</sub>-montmorillonite is remobilized before aluminum dissolution is observed (Figure 6e,f), indicating the sorption of cadmium on the outer surface of the aluminum hydroxide lattice.

**Relevance to Soil Remediation.** Natural soils exhibit pH values typically between 4 and 8, some soils also below, and others above this range, depending on the mineral composition, organic matter, base saturation, etc. Acidification of soils may be caused by various natural biotic and abiotic processes, including environmental pollution such as acid rain. Another factor is the set-aside of cultivated land. The latter often means the end of liming which may cause a considerable decrease of soil pH and lead to an increased availability of heavy metals to plant and soil microorganisms.

Adsorption and desorption of zinc and cadmium on Al-montmorillonite and Al<sub>13</sub>-montmorillonite exhibited a hysteresis with respect to pH. This effect is beneficial for remediation purposes as it retards remobilization of sorbed heavy metals upon soil acidification. Al-montmorillonite and Al<sub>13</sub>-montmorillonite show a higher acidic buffer capacity than montmorillonite. The montmorillonites modified by aluminum are more resistant against dissolution after aging 60 weeks, which can be attributed to a gradual rearrangement of the aluminum hydroxides in the interlayer toward higher crystallinity and thus a larger resistance against acidic dissolution. It appears that zinc but not cadmium became partially incorporated into this rearranged structure.

The influence of humic acids on the binding of heavy metals by montmorillonite was investigated under similar experimental conditions in ref 32. Humic acids are major constituents of soils and interact extensively with heavy metals (33–35). They can sorb on mineral surfaces and, in this role, may offer additional, high-affinity complexation sites for metal cations (36–38). Lothenbach (32) found that humic acids sorbed partially on the surfaces of montmorillonite, Al-montmorillonite, and Al<sub>13</sub>-montmorillonite. This effect, however, did not compromise the efficiency of the mineral binding agents for heavy metal immobilization. In combination, the binding capacities of humic acids and montmorillonite compounds were found to be approximately additive. However, low-molecular-weight, less aromatic humic substances (i.e. fulvic acids) are less likely to sorb on mineral surfaces (39, 40) and are therefore more likely to increase dissolved heavy metal concentrations (41, 42).

We may conclude that the ability of Al-montmorillonite and Al<sub>13</sub>-montmorillonite to adsorb and to incorporate zinc can be used for the gentle remediation of soils polluted by heavy metals particularly as the pH hysteresis of the sorption edges of the binding agents provide additional resistance against metal remobilization due to acidification.

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