THE REMOBILIZATION OF METALS FROM IRON OXIDES AND SEDIMENTS BY METAL-EDTA COMPLEXES

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Abstract. Synthetic chelating agents such as EDTA form strong complexes with heavy metals and therefore have the potential to remobilize metals from sediments and aquifers. In natural waters EDTA is present almost exclusively in the form of metal-complexes. Therefore, remobilization of metals is always a metal-metal-EDTA exchange reaction. We have investigated, to our knowledge for the first time, the remobilization of metals from the surface of synthetic iron oxides and from a river sediment by different metal-EDTA complexes. The metals are exchanged as follows:

$$\mathrm{MeEDTA_{dissolved}} + \mathrm{Me^{*}_{adsorbed}} \rightarrow \mathrm{Me^{*}EDTA_{dissolved}} + \mathrm{Me_{adsorbed}}$$

The order of the remobilization rate of Zn^{2+} from goethite is CaEDTA > Fe(III)EDTA, reflecting the slow exchange reaction of Fe(III)EDTA. For the remobilization of Pb^{2+} from goethite, the rate was found to be Fe(III)EDTA > CaEDTA > ZnEDTA. Here, Fe(III)EDTA has surprisingly the fastest exchange rate. Only very limited remobilization of Pb^{2+} is possible from hydrous ferric oxide at pH 8 due to the very strong adsorption of Pb^{2+}. The order of remobilization of Zn^{2+} from a natural river sediment was found to be CaEDTA > CuEDTA > Fe(III)EDTA. The remobilization rate of Zn^{2+} with Fe(III)EDTA is only 12% of the rate with CaEDTA, illustrating the importance of EDTA speciation for assessing remobilization.

Keywords: complexation, desorption, EDTA, goethite, lead, remobilization, river sediment, zinc

1. Introduction

Metal ions are strongly bound to iron and manganese oxides at neutral pH. Several processes are capable of releasing metal ions back into solution. These processes are of special interest concerning the mobility of toxic trace elements in groundwater and surface water systems. Important remobilization processes include (Coughlin and Stone, 1995): (1) acidification, (2) competitive adsorption of other metal ions or anions, (3) reductive and non-reductive dissolution of the solid phase, and (4) complexation of metal ions by ligands. In recent years, the remobilization of metals by synthetic anthropogenic chelating agents has received much attention. The use of EDTA (ethylenediaminetetraacetic acid) and NTA (nitrilotriacetic acid) has especially been questioned because of their potential for increasing the solubilization and remobilization of heavy metals from aquatic sediments (Müller and

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Förstner, 1976) or from aquifer material during the infiltration from river water to groundwater (Hering, 1995).

EDTA is not degraded during conventional wastewater treatment (Kari and Giger, 1995b), but is degraded in rivers by photolysis of the Fe(III)EDTA complex (Kari and Giger, 1995a).

EDTA has been measured in rivers at mean concentrations ranging from 0.01 to 0.1 μM with peak concentrations of up to 0.6 μM (Kari and Giger, 1995a). EDTA can also be present in groundwater originating from infiltration of river water (Bergers and de Groot, 1994; Hering, 1995; Nowack *et al.*, 1995; Grischek *et al.*, 1997). EDTA can increase the dissolved concentration of metal ions by two processes: by dissolution of a solid phase (aluminum-, iron, – or manganese oxides) and by remobilization of adsorbed or precipitated metal ions like Cu, Zn, Pb, or Cd. We define the formation of Fe(III)EDTA (or AlEDTA) as dissolution and not as remobilization. Remobilization in this paper refers to the process where a metal ion that is adsorbed onto or precipitated at the surface of a lattice mineral is solubilized.

Rapid dissolution of iron oxides was observed following injection of PbEDTA and ZnEDTA during a field experiment conducted in a sandy aquifer with a pH between 5 and 6 (Davis *et al.*, 1993). Dissolved Pb and Zn disappeared and dissolved Fe appeared in the groundwater indicating a reaction of the type

$$\text{PbEDTA}_{\text{dissolved}} + \text{FeOOH(s)} \rightarrow \text{Fe(III)EDTA}_{\text{dissolved}} + \text{Pb}_{\text{adsorbed}} \tag{1}$$

Dissolution reaction kinetics are influenced by pH, the iron oxide present and the exchange kinetics of the dissolving metal-EDTA complex (Nowack and Sigg, 1997). At low pH, formation of Fe(III)EDTA is the dominant process. As a result, remobilization of metals is only possible at high pH.

In natural systems, strong organic ligands like EDTA are always present as metal-complexes. Such complexes can have considerably different properties than uncomplexed EDTA. The rates of metal-EDTA exchange reactions strongly depend upon the complexed metal (Margerum *et al.*, 1978; Hering and Morel, 1989; Xue *et al.*, 1995a). For example, CaEDTA exchanges orders of magnitude faster with Zn^{2+} than CuEDTA or Fe(III)EDTA (Hering and Morel, 1989; Xue *et al.*, 1995a). To date, remobilization of heavy metals by EDTA has been studied exclusively with the uncomplexed form of EDTA, Na_2H_2EDTA, or in systems where the speciation of EDTA was not known (Müller and Förstner, 1976; Bryce *et al.*, 1994; Gonsior *et al.*, 1997; Lorenz, 1997; Kedziorek *et al.*, 1998; Yu *et al.*, 1998; Bordas and Bourg, 1998). To our knowledge, there is no investigation focusing on remobilization reactions by metal-ligand complexes.

Which EDTA-complexes can be expected in the environment? Fe(III)EDTA was found to be a major EDTA species in discharge from wastewater treatment plants, contributing 20–90% of total EDTA (Kari and Giger, 1995b). In a recent study concerning EDTA-speciation in several Swiss wastewater treatment plants, Fe(III)EDTA, NiEDTA, and CaEDTA were found to be predominant species in the effluent (Nirel *et al.*, 1998). The speciation of EDTA in a river water, determined by a combination of analytical techniques and equilibrium calculations, was found to be: 32% Fe(III)EDTA, 32% ZnEDTA, 15% Mn(II)EDTA, 13% CaEDTA, 6% NiEDTA and 2% PbEDTA (Nowack *et al.*, 1997). CuEDTA was found to account for less than 1% of total EDTA due to the presence of very strong natural ligands for Cu.

The aim of this study was to investigate the influence of metal complexation by EDTA on metal ion remobilization processes. CaEDTA, ZnEDTA, and Fe(III)EDTA, which have been found to be important in natural waters, have been investigated, and we are studying reactions of the type

$$\mathrm{MeEDTA}_{\mathrm{dissolved}} + \mathrm{Me}^{*}_{\mathrm{adsorbed}} \rightarrow \mathrm{Me}^{*}\mathrm{EDTA}_{\mathrm{dissolved}} + \mathrm{Me}_{\mathrm{adsorbed\ or\ dissolved}} \quad (2)$$

Experimental results will be discussed for both synthetic iron oxides and, on a relative scale, natural river sediment. Additional information will be provided by use of equilibrium calculations involving adsorption onto and dissolution of iron oxides.

2. Experimental Section

2.1. MATERIALS

Goethite (α-FeOOH) was synthesized according to Schwertmann and Cornell (1991) and characterized as described in Nowack and Sigg (1996). It was stored as suspension of 24 g L^{-1} in water. Ferrihydrite (HFO) was synthesized freshly for each experiment by rapid hydrolysis of an acidic 1 mM $Fe(NO_3)_3$ solution. It was aged for 14–20 hr at pH 7–8 prior to use. HFO surface properties have been described previously (Nowack *et al.*, 1996).

2.2. DESORPTION EXPERIMENTS WITH SYNTHETIC OXIDES

Oxide-suspension (0.08–0.12 g L^{-1}), ionic medium (0.01 M $NaNO_3$), and HEPES-buffer (4–2(hydroxyethyl)-piperazine-1-ethane-sulfonic acid, 2 mM, pH 8.0 ± 0.1) were added to polyethylene (PE) bottles. For experiments with CaEDTA, additional $Ca(NO_3)_2$ was added to reach a final concentration of 1 mM to ensure a complete formation of the CaEDTA complex. Suspensions were then equilibrated for 1 hr by stirring with a Teflon stirrer at room temperature (22–24 °C). Afterwards 12 μM Zn^{2+} as $Zn(NO_3)_2$ or 0.25 μM Pb as $Pb(NO_3)_2$ was added and equilibrated for 4 hr. Remobilization was initiated by addition of 12 μM Fe(III)EDTA or CaEDTA (Zn-experiments) or 0.7 μM Fe(III)EDTA, CaEDTA, or ZnEDTA (Pb-experiments). For HFO and Pb, an additional experiment involved 1.2 μM Fe(III)EDTA and 0.25 μM Pb. EDTA was always added as 1:1 metal-EDTA complex, either as NaFe(III)EDTA$\cdot 2H_2O$ (Fluka, Switzerland) or preformed from $Na_2H_2EDTA \cdot 2H_2O$ and the metal nitrate. Samples were withdrawn via a PE-syringe and filtered through 0.2 μm cellulose nitrate filters (Sartorius). The filtrate was acidified and analyzed for Zn by ICP-AES and Pb by graphite furnace AAS. The sample pH was measured by a Metrohm pH-Meter calibrated with standard buffers.

2.3. NATURAL RIVER SEDIMENT

Sediment was collected from the Glatt river, a small stream in Switzerland that receives a high input of cleaned wastewater (up to 50% of the discharge in summer). It was freeze-dried, ground and sieved. Sediment with a grain size <200 μm was then used for experiments. Particles from the Glatt were found to contain 10–50 mg g^{-1} Fe, 1–3 mg g^{-1} Mn, 80–130 mg g^{-1} Ca, 0.2–0.8 mg g^{-1} Zn, 20–130 μg g^{-1} Cu, and 100–400 μg g^{-1} Pb (Müller, 1989). A detailed characterization of the mineral and surface properties of the sediment were not performed because our intention was to interpret and discuss the results of the experiments on a relative scale. For each experiment 5 g of sediment was placed in 100 mL polypropylene (PP) bottles and 50 mL of Glatt water (pH 8) was then added in addition to various concentrations of different metal-EDTA complexes (uncomplexed EDTA, CaEDTA, ZnEDTA or Fe(III)EDTA) at different concentrations (0.7 μM, 3.4 μM, and 17 μM EDTA complexes) and equilibrated for 24 hr. For the kinetic experiments, 3.4 μM EDTA was added. The final pH was at 8.0 ± 0.2 in all experiments. Suspensions were agitated on a shaking machine for different time periods at a temperature of 25 °C. Samples were centrifuged (5 min, 10 000 rpm) and the supernatant was filtered through acid-precleaned 0.1 μm cellulose nitrate filters (Sartorius) prior to analysis. The filtrate was then acidified and analyzed for Mg, Ca, Mn and Zn by ICP-AES. Cu concentrations were determined by graphite furnace AAS.

3. Results and Discussion

3.1. REMOBILIZATION OF ZN FROM OXIDES

Less than 5% of Zn^{2+} remained in solution if equilibrated with hydrous ferric oxide (HFO) or goethite at pH 8. After addition of CaEDTA or Fe(III)EDTA, Zn reappeared in solution, indicating that a remobilization process was occurring (Figure 1). In contrast to Zn^{2+}, ZnEDTA does not adsorb onto HFO at pH 8 (Nowack *et al.*, 1996) and is therefore present in the aqueous phase. All dissolved Zn was therefore considered to be ZnEDTA because without a change in pH, no desorption of free Zn^{2+} is expected. The exchange reactions can be described by Equations (3) and (4):

$$\mathrm{Zn_{adsorbed}} + \mathrm{CaEDTA} \rightarrow \mathrm{ZnEDTA} + \mathrm{Ca_{dissolved}} \tag{3}$$

$$\mathrm{Zn_{adsorbed}} + \mathrm{Fe(III)EDTA} \rightarrow \mathrm{ZnEDTA} + \mathrm{Fe_{adsorbed}} \tag{4}$$

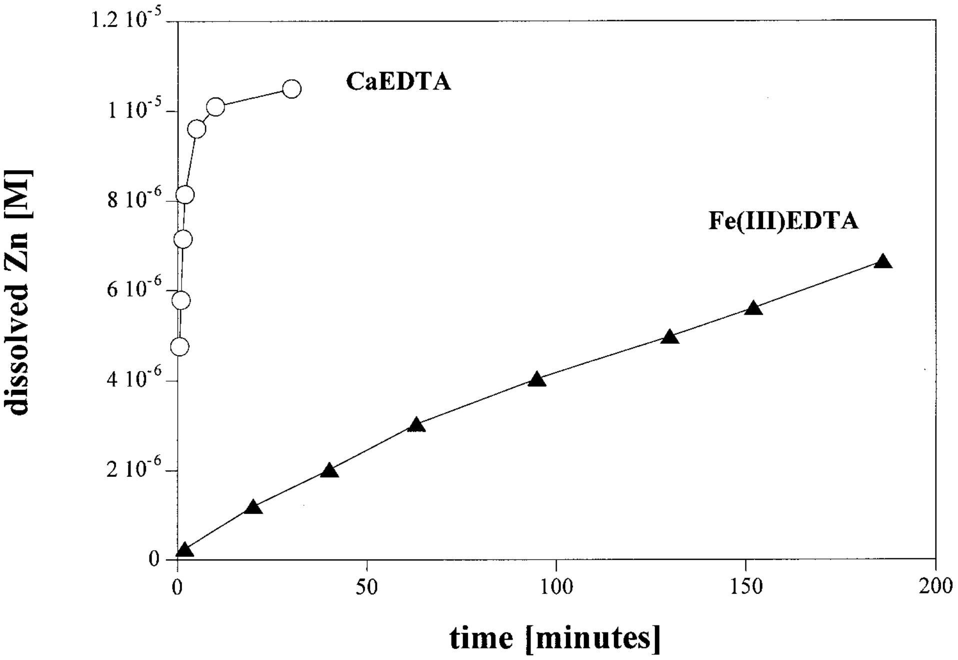

Figure 1. Remobilization of 12 μM Zn from HFO by 12 μM CaEDTA or 12 μM Fe(III)EDTA at pH 8.0.

ZnEDTA (logK 16.5) is formed in experiments using either CaEDTA (logK 10.6) or Fe(III)EDTA (logK 25.2). Although Fe(III) forms much stronger complexes with EDTA than Zn^{2+}, formation of ZnEDTA occurs at pH 8. Equilibrium calculations have been performed in order to better understand this phenomenon.

The concentration of Fe(III)EDTA is governed by dissolution of the solid phase, in our case hydrous ferric oxide (HFO). The speciation of EDTA was calculated for a system with HFO present, 1 μM EDTA and 1 μM Zn^{2+}. Calculations were performed using the speciation program MacμQL (Müller, 1993). HFO solubility, stability constants of the EDTA-complexes and stability constants of the metal-hydroxo complexes were obtained from the Critical database (Martell *et al.*, 1997). Adsorption of Zn^{2+} onto HFO was also included in the model (Dzombak and Morel, 1990). Results of the calculations are shown in Figure 2. Without EDTA present, all Zn^{2+} is adsorbed onto HFO above pH 7 (dotted line). In the presence of EDTA, adsorption of Zn^{2+} is suppressed at high pH (dashed line). Below pH 6, Fe(III)EDTA is the primary EDTA species present in solution, between pH 6 and 7 ZnEDTA and Fe(III)EDTA are of similar importance, and above pH 7 ZnEDTA becomes the prevalent species. The calculation supports the experimental results that at low pH dissolution of the oxide (= formation of Fe(III)EDTA) by metal-EDTA complexes is the dominant process (Davis *et al.*, 1993; Nowack and Sigg, 1997).

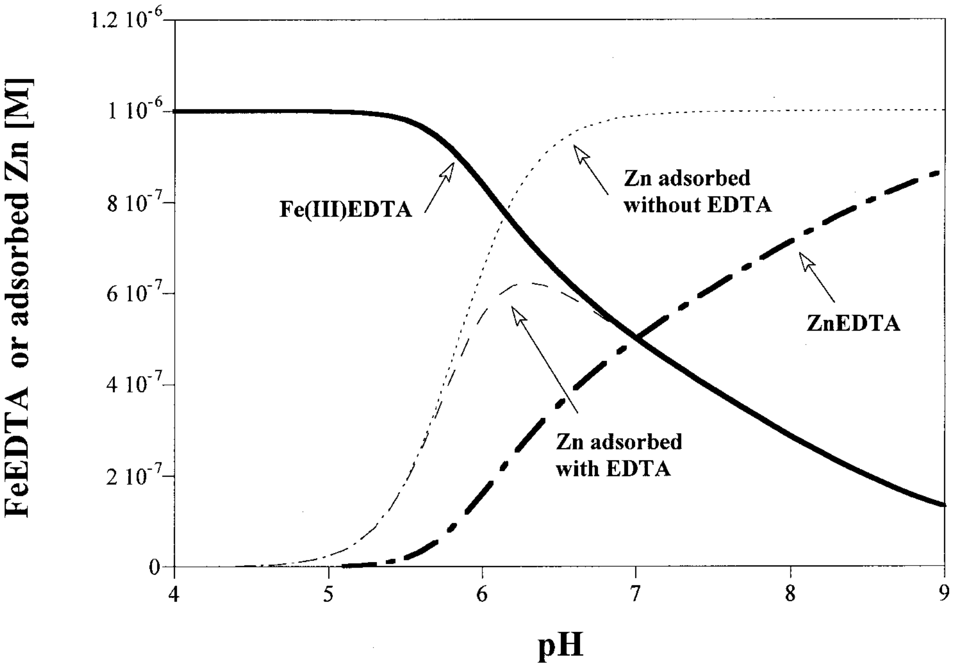

Figure 2. Calculated speciation in the system Zn-EDTA-HFO as a function of pH. Both adsorption of Zn and dissolution of HFO have been considered. The dotted line shows the adsorption of Zn in the absence of EDTA.

If 1 μM Fe(III)EDTA and 1 μM Zn^{2+} are added to HFO at pH 5, then the system is already at equilibrium and the speciation of EDTA and Zn does not change (Figure 2). However, if 1 μM Fe(III)EDTA is added to the system at pH 8 (where 1 μM Zn^{2+} is initially adsorbed onto HFO), then the equilibrium speciation is predicted to be 0.3 μM Fe(III)EDTA and 0.7 μM ZnEDTA. Therefore, a partial remobilization of Zn^{2+} is expected to occur by formation of ZnEDTA. Some Zn^{2+} will remain adsorbed even in the presence of 1 μM EDTA. We can see in Figure 1 that indeed not all Zn could be desorbed in the presence of Fe(III)EDTA after a time of 190 min. The same calculation for CaEDTA shows that all Zn should be desorbed at pH 8. Indeed, greater than 90% of Zn was recovered in experiments with CaEDTA.

The combination of two factors determines the shape of the curves in Figure 2: the strength of the adsorption of the metal and the solubility product of the iron oxide. A metal which forms strong surface complexes favors the formation of Fe(III)EDTA at high pH. An iron oxide with a lower solubility than HFO, for example goethite, reduces the stability of Fe(III)EDTA at high pH, resulting in Zn remobilization at a lower pH.

The equilibrium calculations show that both CaEDTA and Fe(III)EDTA are able to remobilize Zn at pH 8. These calculations, however, say nothing about

TABLE I

Metal exchange kinetics in aqueous solution: MeEDTA + Me* → Me*EDTA + Me

Me	Me*	Rate constant (M^{-1} s^{-1})	Reference
H	Zn	10^9	Margerum *et al*., 1978
Ca	Zn	1100	Xue *et al*., 1995a
Fe(III)	Zn	10.3	Xue *et al*., 1995a
H	Pb	3×10^9	Margerum *et al*., 1978
Ca	Pb	43400	Nowack, 1997
Zn	Pb	57	Nowack, 1997
Fe(III)	Pb	1.2	Nowack, 1997

the kinetics of this process on first sight. Figure 1 reveals that there is an enormous difference in the rate of Zn remobilization by CaEDTA and Fe(III)EDTA. While Zn desorption with CaEDTA is almost instantaneous, the reaction with Fe(III)EDTA is much slower. This is in agreement with the much faster exchange rate of Zn^{2+} with CaEDTA with compared to Fe(III)EDTA (Table I). Zn^{2+} reacts about 100-times faster with CaEDTA than with Fe(III)EDTA. The rate-limiting step in the homogeneous reaction is the dissociation of the metal-EDTA complex (Margerum *et al*., 1978; Hering and Morel, 1989). Fe(III)EDTA dissociates very slowly and therefore has the slowest exchange rate (Xue *et al*., 1995a).

Uncomplexed EDTA reacts very rapidly with free Zn^{2+} ions, with a second order rate constant of 10^9 M^{-1} s^{-1} (Margerum *et al*., 1978). The second order rate constant for the exchange of CaEDTA with Zn^{2+} is 1100 M^{-1} s^{-1} (Xue *et al*., 1995a). Therefore, complexation of Zn^{2+} by free EDTA is 6 orders of magnitude faster than by CaEDTA. Similar ratios are found for other metal-EDTA complexes. Because EDTA is always present in natural waters as a metal-complex, the slow exchange of metals will determine the remobilization kinetics. EDTA complexes with metals having very slow water exchange rates such as Co(III) or Cr(III), will be ineffective at remobilizing metals on a time scale of several days.

3.2. REMOBILIZATION OF PB FROM OXIDES

Suspensions of Pb^{2+} equilibrated at pH 8.0 with goethite or HFO had no detectable dissolved Pb^{2+} concentration. After addition of 0.7 μM EDTA in the form of different complexes, remobilization of Pb was observed (Figure 3). In contrast to Pb^{2+}, PbEDTA does not adsorb onto iron oxides at pH 8 (Nowack *et al*., 1996). Again, the remobilization rate was dependent upon the added metal-complex. The reaction

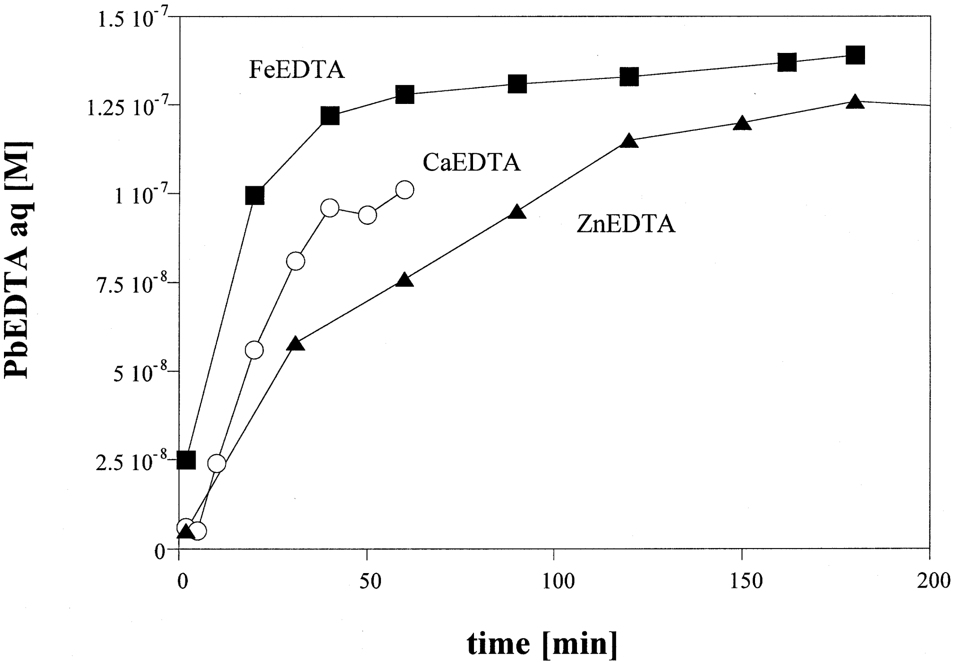

Figure 3. Remobilization of 0.24 μM Pb from goethite by 0.7 μM CaEDTA, ZnEDTA or Fe(III)EDTA at pH 8.

rate decreased in the order Fe(III)EDTA > CaEDTA > ZnEDTA. It is surprising that Fe(III)EDTA remobilizes Pb^{2+} faster than CaEDTA because the corresponding exchange reaction in solution follows the order CaEDTA > > ZnEDTA > Fe(III)EDTA (Table I). The reaction of CaEDTA with Pb^{2+} in homogeneous solution is more than 30 000-times faster than the reaction of Fe(III)EDTA with Pb^{2+}. Therefore, we would expect that Fe(III)EDTA remobilizes Pb^{2+} at a much slower rate than CaEDTA. However, only small differences between the metal-EDTA complexes were observed. This indicates that the exchange reaction is not the rate-limiting step. One possible explanation is that the coordination of Pb^{2+} to the surface changes the exchange kinetics of Pb^{2+} and the rate-limiting step involves detachment of Pb^{2+} from the surface.

Of the 0.25 μM Pb^{2+} that was initially adsorbed onto goethite, 0.14 μM could be desorbed using 0.7 μM Fe(III)EDTA. If the same amount of Pb^{2+} was initially adsorbed onto HFO, no remobilization was observed, even after 20 days. For a higher Fe(III)EDTA concentration (1.2 μM Fe(III)EDTA and 0.25 μM Pb^{2+}), approximately 0.02 μM PbEDTA was observed in solution after few hours (Figure 4). No further change in dissolved PbEDTA concentration was observed over several days. The differing behavior of the two oxides can be explained with the help of equilibrium calculations. Model calculations considered adsorption of Pb^{2+} onto HFO (Dzombak and Morel, 1990) or goethite (Palmqvist *et al.*, 1997), adsorption

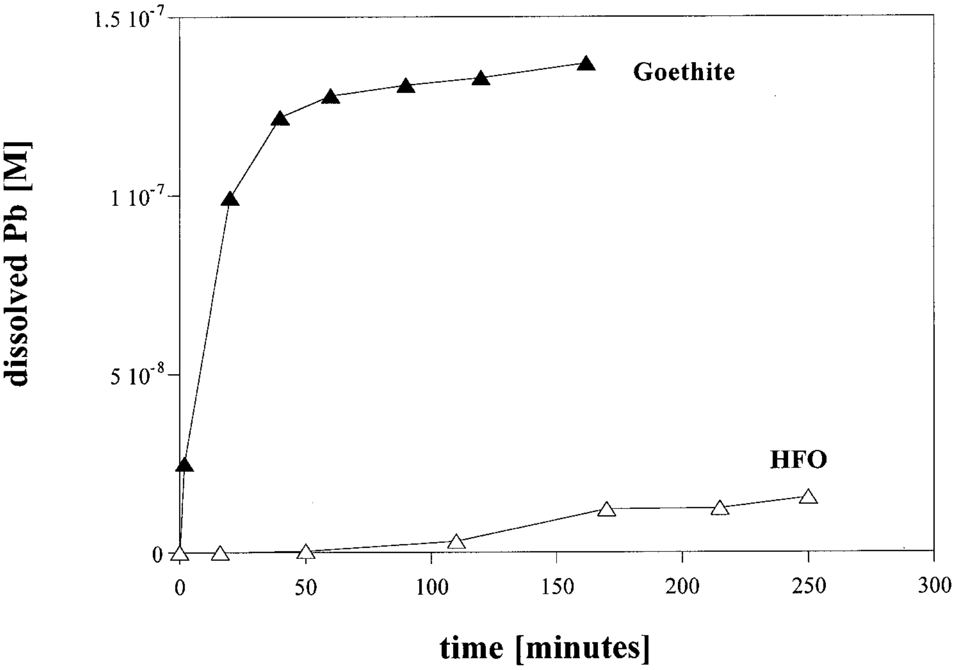

Figure 4. Remobilization of 0.25 μM Pb from goethite and HFO at pH 8 by 0.7 μM (goethite) or 1.2 μM Fe(III)EDTA (HFO).

of PbEDTA and Fe(III)EDTA onto goethite (Nowack and Sigg, 1996) and HFO (Nowack *et al.*, 1996) and solution equilibria (hydrolysis of Pb^{2+}, complexation of Pb^{2+} and Fe(III) by EDTA, and solubility of HFO or goethite). All stability constants were obtained from Martell *et al.* (1997). The calculation for 1 μM EDTA and 1 μM Pb^{2+} illustrates how the type of oxide has a pronounced influence on the speciation of EDTA (Figure 5). In the presence of goethite, PbEDTA is the prevalent Pb species at pH above 5.5, while in the presence of HFO, PbEDTA only accounts for more than 10% of Pb^{2+} above pH 8. The very strong adsorption of Pb^{2+} to the surface of HFO stabilizes Fe(III)EDTA. If the calculation is performed with the concentrations used in the experiments that are shown in Figure 4 (0.25 μM Pb^{2+} and 1.2 μM EDTA), the predicted PbEDTA concentration at pH 8 is 0.019 μM with HFO and 0.25 μM with goethite. Therefore, the dissolved Pb concentration found in the HFO experiment (0.02 μM) is in very good agreement with the calculated concentration. For goethite, the calculation predicts that all Pb should be desorbed under the conditions of Figure 4. However, only 60% of the Pb could be desorbed within 3 hr. The discrepancy between calculated and experimental results is possibly due to the existence of a small fraction of surface sites that have a very high affinity for Pb^{2+}. The adsorption of Fe(III)EDTA onto goethite can be neglected. At pH 8 about 0.08 μM FeEDTA can be adsorbed onto

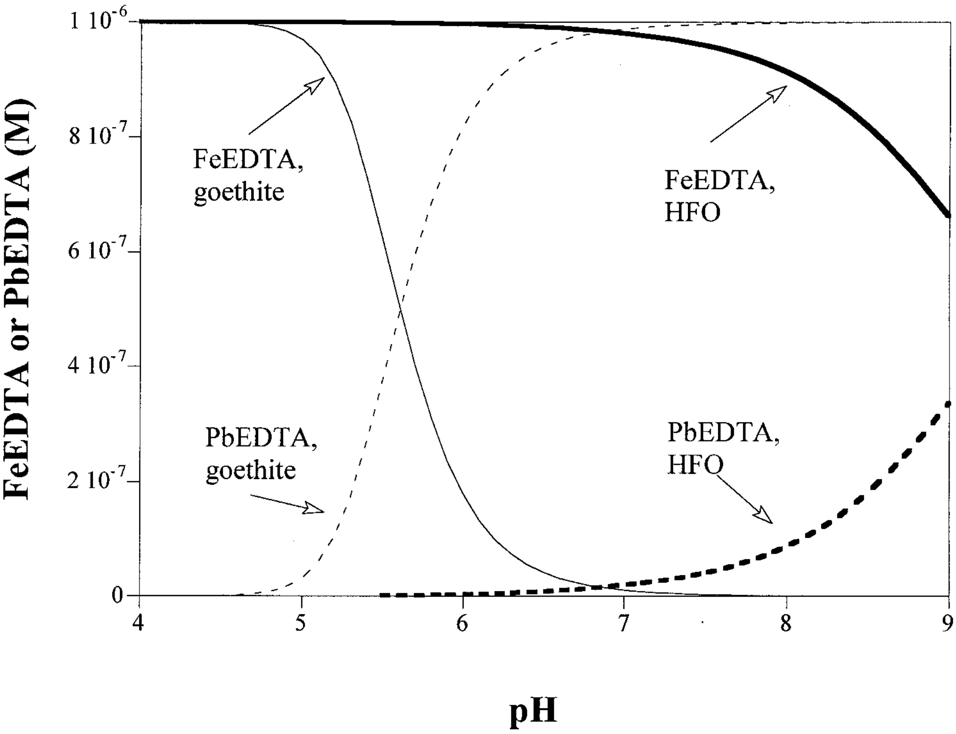

Figure 5. Calculated speciation in the system Pb-EDTA-goethite and Pb-EDTA-HFO (1 μM Pb and EDTA, 0.1 g L^{-1} goethite or HFO). Both adsorption of Pb and dissolution of HFO or goethite have been considered.

0.11 g L^{-1} goethite (Nowack *et al.*, 1996), which is 6% of the added 1.2 μM FeEDTA.

We can learn from these calculations that if we want to predict the possibility of a remobilization process, we have to include the adsorption of the metals to the surface into the model. If a particular reaction is not observed, as in the case with HFO/Pb^{2+}/FeEDTA, equilibrium calculations can tell us whether this is caused by very slow exchange reactions or by the thermodynamic equilibrium which does not allow a remobilization.

3.3. RIVER SEDIMENT

Figure 6 shows the remobilization of Mn, Zn and Cu by EDTA from the Glatt river sediment after 24 hr. The concentration of remobilized metals without EDTA addition (6 μM Mn, 0.6 μM Zn, and 0.09 μM Cu) was subtracted from all measurements. Figure 6 depicts the influence of increasing EDTA concentration (NaEDTA and CaEDTA) on the remobilization of Cu, Zn, and Mn. Addition of uncomplexed EDTA (NaEDTA) to the Glattwater containing about 1.5 mM Ca immediately results in the rapid formation of CaEDTA. Therefore, no differences are expec-

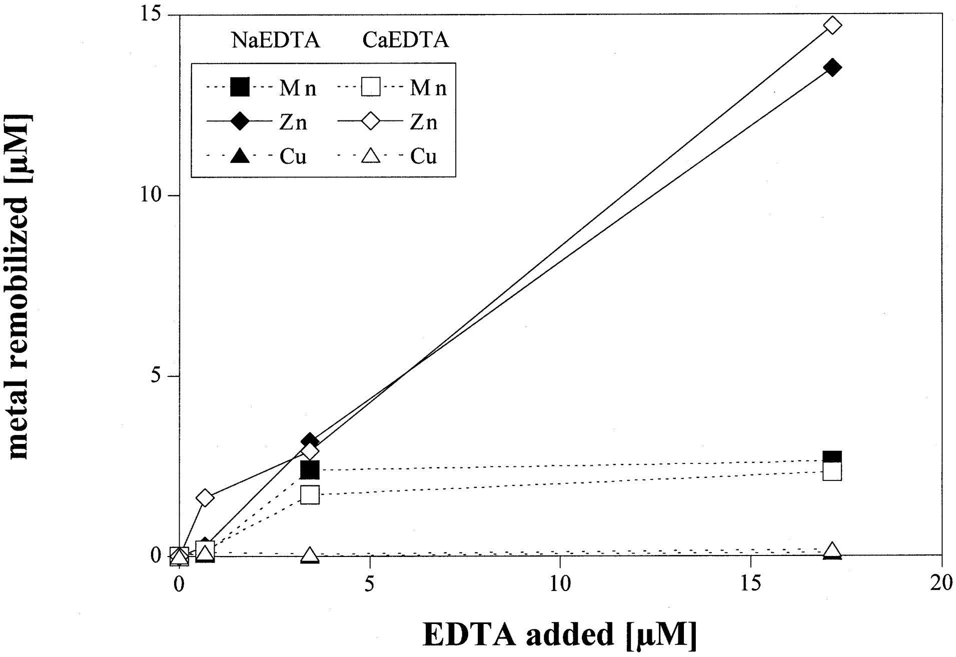

Figure 6. Remobilization of metals after 24 hr by EDTA in Glatt river sediment-water suspensions at pH 8. 0.68, 3.42 and 17.12 μM EDTA was added as NaEDTA or CaEDTA.

ted between addition of uncomplexed EDTA and CaEDTA. The Zn concentration is directly proportional to the EDTA concentration, suggesting remobilization by formation of ZnEDTA. Some remobilization of Mn is observed (compared to blank) but no significant Cu desorption was detected. The total amount of Zn in the system (170 μM) is about 10-times higher than the remobilized amount with the highest EDTA concentration (17 μM). These results are in agreement with other investigations which show that EDTA primarily remobilizes Zn (Lorenz, 1997; Twachtmann *et al.*, 1998). However, our goal in this part of the investigation was not to determine which metals are remobilized but how EDTA speciation influences the rate of remobilization.

The time courses for remobilization of Zn by different metal-EDTA complexes are shown in Figure 7. All four metal-EDTA complexes that were tested were able to remobilize Zn from the sediment, but at different rates.

$$\mathrm{Zn_{adsorbed}} + \mathrm{MeEDTA} \rightarrow$$

$$\mathrm{ZnEDTA} + \mathrm{Me_{adsorbed}}\ (\mathrm{Cu},\ \mathrm{Fe})\ \text{or}\ \mathrm{Me_{dissolved}}\ (\mathrm{Ca},\ \mathrm{Na}) \qquad (5)$$

Figure 7 shows clearly that Fe(III)EDTA and CuEDTA react much slower with adsorbed Zn in the sediment than CaEDTA. This is especially true after a short reaction time, where the amount of Zn remobilized by NaEDTA (actually CaEDTA in

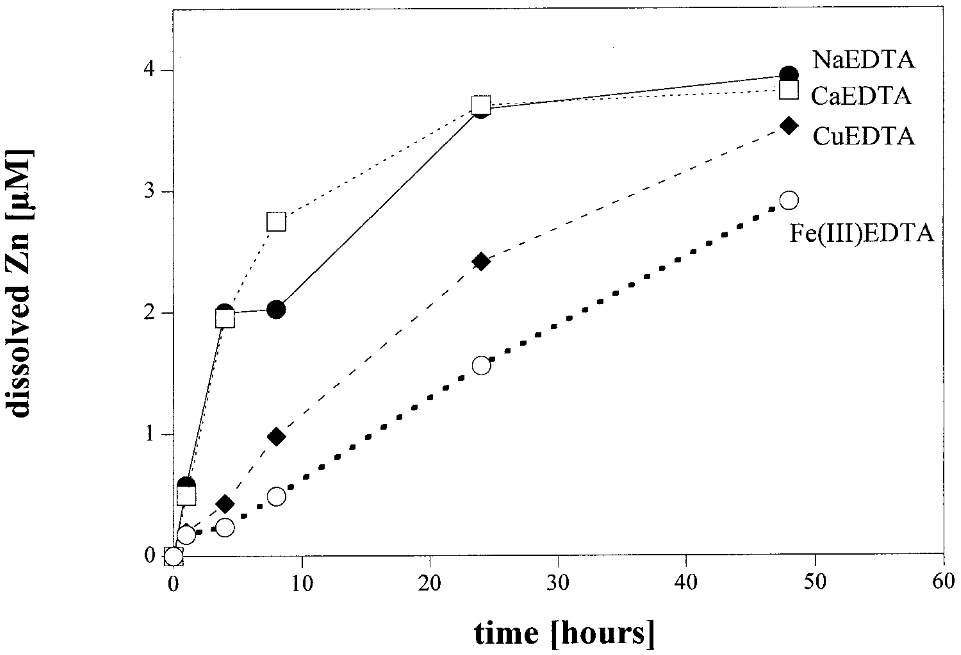

Figure 7. Remobilization of Zn by EDTA in Glatt river sediment-water suspensions at pH 8. 3.42 μM EDTA was added as NaEDTA, CaEDTA, CuEDTA, or Fe(III)EDTA.

TABLE II

Remobilization rate of Zn from Glatt sediment by 3.4 μM EDTA in the first 4 hr. Remobilization is expressed as μM of Zn remobilized per hour

Species	Zn remobilized	
	μM hr^{-1}	% of rate for NaEDTA
NaEDTA	0.50	100
CaEDTA	0.49	98
CuEDTA	0.11	22
Fe(III)EDTA	0.06	12

the Glattwater) or CaEDTA is significantly higher than by CuEDTA or Fe(III)EDTA. Table II compares remobilized Zn for the first 4 hr. The rate for CuEDTA and Fe(III)EDTA is only 22 and 12% of the rate for NaEDTA or CaEDTA.

The order of the remobilization rate NaEDTA CaEDTA > CuEDTA > Fe(III)EDTA is expected based on the known exchange rates of the metal-EDTA complexes.

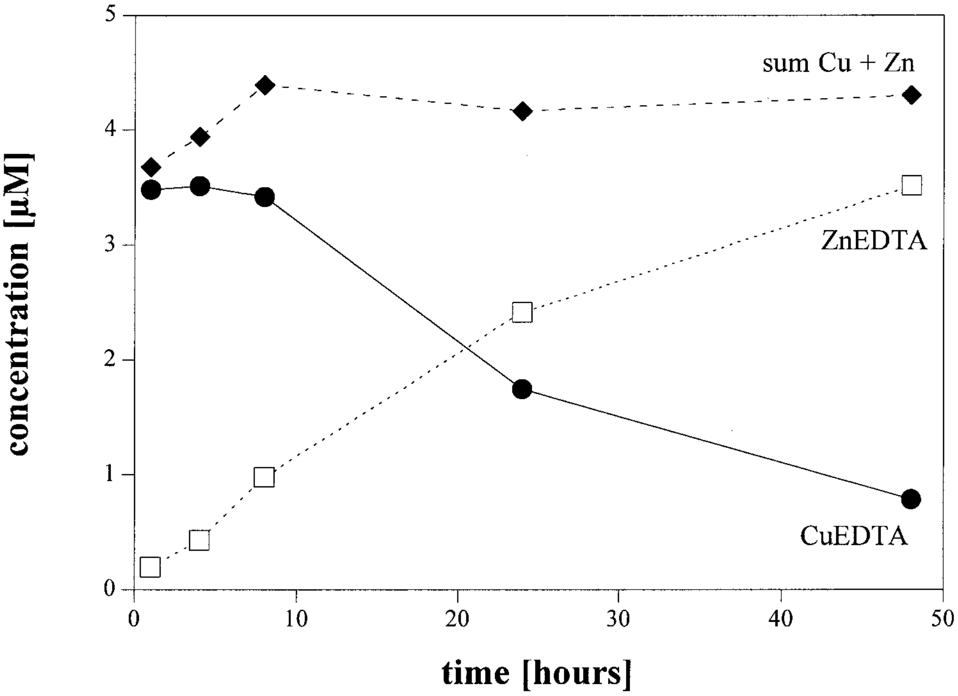

Figure 8. Remobilization of Zn by 3.42 μM CuEDTA (and parallel disappearance of dissolved Cu) in Glatt river sediment-water suspensions at pH 8.

Figure 8 shows a timecourse for dissolved Cu and Zn when CuEDTA is added to the sediment. Here dissolved Cu decreases over time and dissolved Zn appears in solution. The sum of dissolved Cu and Zn remains constant following a small initial increase. The reaction in suspension can be formulated as follows:

$$\mathrm{Zn_{adsorbed} + CuEDTA_{dissolved} \rightarrow ZnEDTA_{dissolved} + Cu_{adsorbed}} \tag{6}$$

Although CuEDTA (logK 18.78) is a stronger complex than ZnEDTA (logK 16.5), the exchange reaction goes in the direction to ZnEDTA. Again, direct evaluation of the remobilizing capacity of a complex is not possible when considering the stability constants of the metal-EDTA complex alone. The equilibrium concentration of dissolved Cu is determined by the type of iron oxide and surface sites for Cu present in the sediment. In the sediment Cu is probably bound as strong organic complex which is able to displace Cu from CuEDTA:

$$\mathrm{CuEDTA + L_{ads} \rightarrow CuL_{ads} + EDTA} \tag{7}$$

Free EDTA then remobilizes Zn:

$$\mathrm{EDTA + Zn_{ads} \rightarrow ZnEDTA} \tag{8}$$

Natural ligands in the river Glatt were found to have a much higher affinity for Cu than Zn (Xue *et al*., 1995b). In soils, Cu speciation is also governed by organic Cu-complexes (Baker, 1990). These natural organic Cu-complexes are apparently so strong that EDTA is not able to displace Cu from the complex. Cu bound to these ligands is therefore not susceptible to remobilization by EDTA.

4. Conclusions

Our work demonstrates that the remobilization of metals is determined by two processes:

- the speciation at equilibrium which is mainly governed by the dissolution of oxides (formation of Fe(III)EDTA) and the adsorption of metals to the oxide surface.
- the kinetics of the exchange reaction

$$\text{MeEDTA} + \text{Me}^* \rightarrow \text{Me}^*\text{EDTA} + \text{Me}_{\text{ads}}$$

If a large fraction of EDTA is present in the form of complexes that have slow exchange kinetics, for example Fe(III)EDTA, NiEDTA, Cr(III)EDTA, or Co(III)EDTA, then remobilization of adsorbed metals can be slow, even in the presence of high EDTA concentrations.

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