Influence of Natural and Anthropogenic Ligands on Metal Transport during Infiltration of River Water to Groundwater

BERND NOWACK,*,† HANBIN XUE, AND LAURA SIGG

Swiss Federal Institute for Environmental Science and Technology (EAWAG), and Swiss Federal Institute of Technology (ETH), CH-8600 Dübendorf, Switzerland

The behavior of dissolved metals, the anthropogenic ligands EDTA and NTA, and the natural ligands for Cu and Zn during infiltration of river water to the adjacent aquifer was investigated at the Glatt River field site (Switzerland). The speciation of EDTA was determined by a combination of experimental methods and of equilibrium calculations. The speciation of EDTA that behaves conservatively with respect to its total concentration changes on the infiltration path. The main EDTA species in the river water are Zn–EDTA, Ca–EDTA, and Fe(III)–EDTA and in some of the groundwaters Mn(II)–EDTA. The speciation of EDTA is strongly influenced by the presence of natural organic ligands for Cu and Zn that bind a large fraction of these metals, even in groundwater. Ni–EDTA is a less significant species than expected from equilibrium calculations. Fe(III)–EDTA is not in equilibrium with other metals due to its slow exchange kinetics. The fraction of EDTA that is present as Fe(III)–EDTA decreases from the river with 35% to 11% in groundwater, within a residence time of about 8 days. This decrease indicates that exchange reactions of the type: Fe(III)–EDTA + Me (ads or aq) → MeEDTA + Fe(III) take place in the pH range of 7–8. Remobilization of metals is therefore possible under these conditions.

Introduction

A significant part of the drinking water of Switzerland is pumped from shallow groundwater resources in quaternary glaciofluvial sediments. A large fraction of this groundwater is recharged by infiltration from rivers, to a minor extent from precipitation. The quality of the groundwater is therefore a direct consequence of the quality of the river water and of the processes taking place during the infiltration. Pollution can occur either on a short time scale after an accident or continuously. The rising diffuse pollution of the environment may cause problems with the quality of the drinking water, for example, with respect to heavy metals.

It has often been questioned whether anthropogenic organic ligands may increase the concentration of dissolved metals in the groundwater (*1–3*). Remobilization of metals that are immobilized in the first few meters of the infiltration zone is a possible hazard. EDTA (ethylenediaminetetraacetic acid) is one of the most widely used organic ligands in industry that is applicated, for example, in paper manufacturing, electroplating, and the photographic industry, as a powerful

complexing agent for metals like Ca, Zn, or Fe(III). EDTA is not degraded in sewage treatment plants and is present in the effluents with concentrations up to 18 μM (*4*). EDTA has been measured in groundwaters (*5*), lake waters (*6*), and rivers (*7*) with typical concentrations between 10 and 100 nM. Peak concentrations of up to 0.6 μM have been found in the river Glatt (*7*).

The reactions of EDTA in groundwater involve adsorption to iron and aluminum oxides (*10, 11*) and dissolution of iron oxides (*12, 13*). Davis et al. (*2, 3*) and Kent et al. (*8*) have observed the formation of Fe–EDTA and a slight retardation due to adsorption in studies on mobility of metal–EDTA complexes (Zn, Cu, Ni, Pb) with large-scale tracer tests. Bourg et al. (*9*) found that a pulse of EDTA was able to react with aquifer material and to dissolve adsorbed metals. These reactions have been investigated either in column systems in the laboratory (*9, 12, 13*) or in tracer tests (*2, 3, 8*), but no data are available for natural systems. In field systems, natural organic ligands are always present and have also to be considered, too, as they change the speciation of the metals. Such ligands have been proposed to account for the high mobility of Cu in aquifers (*15*).

The aim of this study was to examine the effects of the two anthropogenic ligands EDTA and NTA and of natural organic ligands on speciation and mobility of trace metals in an infiltration system. The investigated infiltration site of Glattfelden on the Glatt River, Switzerland, has a steady input of both EDTA and natural ligands to the metal-contaminated infiltration zone. Numerous information on pollution of the river (*16*); geochemical changes and annual cycles of metals like Mn, Cd, or Cu (*15, 17–20*); and behavior of organic compounds (*7, 21, 22*) is available.

We determined the concentration of total EDTA and the fraction of Fe–EDTA, and simultaneously the speciation of Cu and Zn, as well as changes of their speciations during infiltration. Based on the measured parameters, the speciation of EDTA and the dissolved heavy metals in the presence of natural organic ligands are evaluated by equilibrium calculations. Then, we compare and discuss the effects of EDTA, NTA, and natural ligands on the remobilization of trace metals.

Methods

Field Site. The field site of Glattfelden is located in the lower Glatt Valley, Switzerland. In this region, the river Glatt infiltrates over a distance of about 5 km into a quaternary aquifer composed of layers of gravel and sand containing very little organic carbon (<0.1%) (*15*). At Glattfelden, the river Glatt contains about 20% effluent from several wastewater treatment plants, which are the main sources of pollutants for the river. The water from the river infiltrates into the uppermost part of the aquifer with an average flow velocity of 4–5 m d^{-1} (*23*).

The site is equipped with observation wells that allow sampling at different depths and distances from the river. The wells are lined with hard PVC pipes (diameter 5 cm). Figure 1 shows the situation of the site with the wells used in this study. The aquifer consists of three layers. The top layer is freshly infiltrated river water, the middle layer is water that was infiltrated upstream of the test site, and the lower layer consists of groundwater that is not affected by infiltration.

Sample Collection. Samples were collected from the river and from the groundwater wells in March and July 1995. Samples from the river were taken by a 4900 portable contaminant sampler from Manning Products. The sampler

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* Corresponding author fax: (410)516-8996.
† Present address: Department of Geography and Environmental Engineering, The Johns Hopkins University, Baltimore, MD 21218.
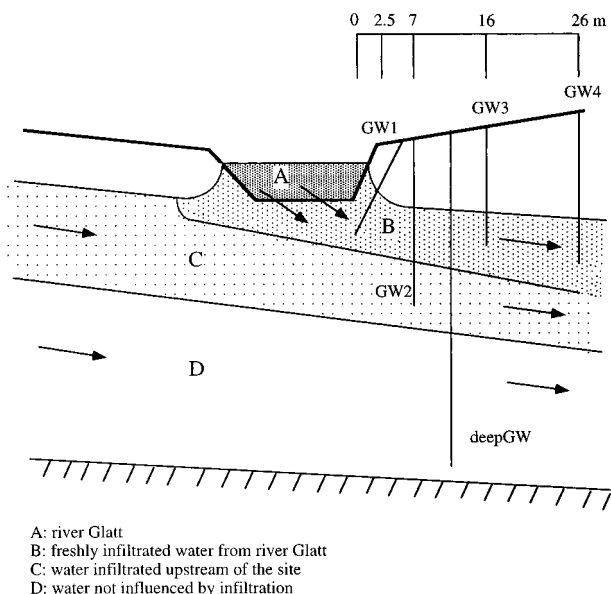
A: river Glatt
B: freshly infiltrated water from river Glatt
C: water infiltrated upstream of the site
D: water not influenced by infiltration

FIGURE 1. Cross-sectional view of the infiltration site with the groundwater flow and the observation wells according to Hoehn et al. (20).

was cleaned by pumping for at least 20 cycles 0.01 M HNO_3 through the tube. The bottles were soaked for 48 h in 0.01 M HNO_3 and rinsed with Nanopure water. The stainless steel end of the tube was removed, and the end was fixed on a stone to hold the inflow under water. Prior to the sampling, river water was pumped through the tube for at least five cycles. For the sampling of the Glatt, every 15 min a sample of 150 mL was taken, and six samples were collected together in one bottle (1.5-h composite sample). A total of 39 samples was taken. Groundwater samples from well GW1 were taken by a second sampler (same type as for the river). The autosampler tube was introduced together with a submerged pump (Whale) into the well. The pump was operated with a low flow (0.5−1 L/min) during the whole sampling. This lead to a steady flow of fresh water toward the well. The autosampler took a sample every 30 min, and six samples were collected in a bottle (3-h composite sample). A total of 57 samples was taken.

Samples from the wells GW2, GW3, and GW4 and the deep groundwater (deepGW) were taken by submerged pumps (Whale). The pumps were cleaned in the lab by pumping 0.01 M HNO_3 for at least 30 min. Prior to the sampling, groundwater was pumped during 20−30 min to remove old water from the pipe. Samples for metal concentration determination by ICP−MS were taken directly at the outflow of the pump and filtered (0.45 μm, Acrodisc, Gelman Science) on the site into precleaned PE tubes (with added HNO_3 to give a final concentration of 0.1 M). The filters had been soaked for a few days with 0.01 M HNO_3. The first 10−20 mL of the filtrate was discarded. Twelve samples from GW2 and GW3 were taken, four from GW4 and three from deepGW. pH and temperature were measured in the field. The samples for EDTA and metal speciation were transported to the lab every 24 h, under exclusion of light to avoid photolysis of Fe(III)−EDTA.

Analyses. Major and trace metal concentrations were determined by ICP−MS. Blanks with the field procedure for Zn, Cu, and Ni were 2×10^{-8}, 3×10^{-9}, and 3×10^{-9} M, respectively. The blank for Pb was $<2 \times 10^{-10}$ M. Fe was measured by graphite furnace AAS, alkalinity was measured by titration with acid, O_2 was measured by Winkler titration, and chloride was measured by argentometry. NTA was measured by GC after derivatization to the propylester; DOC was measured with a Shimadzu TOC-analyzer.

EDTA and Fe−EDTA were measured as described in Nowack et al. (24). One aliquot of the sample was analyzed for total EDTA; another aliquot was irradiated for 10 min under a mercury lamp (850 Wm^{-2}) to degrade the Fe−EDTA. The samples from July were exposed for 2 h to the full sun if possible. This time is sufficient to photolyse all the Fe-(III)−EDTA (7). The other EDTA species are not degraded by light. Both aliquots were analyzed for EDTA. Fe−EDTA was calculated by the difference from total EDTA and photostable EDTA.

Determination of EDTA was performed by HPLC. All EDTA species were transformed to Fe(III)−EDTA by heating for 3 h with $Fe(NO_3)_3$ at pH 3.3. The complex is separated with tetrabutylammonium bromide as counterion on a Lichrocard 250-4 C18 column with formate buffer as the eluent (pH 3.3, 8% acetonitrile) and is detected by UV at 258 nm.

Ni−EDTA was measured semiquantitatively as described in Nowack et al. (24). The amount of Ni−EDTA is calculated by the difference of total photostable EDTA and "fast reacting" EDTA. Fast reacting EDTA is determined as follows: The irradiated sample is measured without addition of Fe(III) and heating. EDTA or metal−EDTA species flowing through the HPLC column can react with Fe(III), adsorbed on free SiO_2 groups on the column, forming Fe(III)−EDTA. Because Ni−EDTA reacts only slowly with Fe(III), it does not form Fe-(III)−EDTA during elution. Ni−EDTA does not absorb at 258 nm in contrast to Fe(III)−EDTA and is not detected.

Speciation of Cu and Zn. Cu speciation has been determined by catechol ligand exchange and DPCSV (differential pulse cathodic stripping voltammetry), and Zn speciation has been determined by EDTA ligand exchange and DPASV (differential pulse anodic stripping voltammetry), as described elsewhere in detail (25−27). DPCSV and DPASV measurements for the speciation of Cu and Zn were carried out within 1 week of the sample collection. The filtered samples were stored in the dark at 4 °C until use.

Briefly, the method for Cu speciation is based on ligand exchange of added catechol with natural ligands, which are bound to Cu; the Cu catechol complexes formed are determined specifically by DPCSV. $[Cu^{2+}]$ and the complexation parameters are determined from equilibrium calculations with the added catechol. All the stability constants were taken from Martell and Smith (28), except the ones of the natural ligands. DPCSV sensitivity had to be calibrated for each individual water sample from the portion of the titration curve at high concentrations of Cu^{2+}. To obtain a Cu titration curve of a water sample, we spiked a series of subsamples with different Cu concentrations at buffered pH 7.8−8.0. The series was allowed to equilibrate at 20 ± 2 °C overnight. The next day, DPCSV was performed with a hanging mercury drop electrode, an Ag/AgCl reference, and a graphite counter electrode held in a Metrohm 647 VA stand combined with a 646 VA processor. Catechol in optimal concentrations (0.2−1 mM for the groundwater) was added to the samples during DPCSV measurements.

The direct results of these Cu titrations are values of $[Cu^{2+}]$ and Ki[Li], a complexing coefficient that corresponds to the product of the stability constants and natural ligand concentrations. Although natural waters contain a wide range of different ligands with different stability constants, for the sake of comparison, a two-ligand model was generally used to estimate conditional stability constants Ki and total ligand concentrations T[Li], using the FITEQL program (29).

Zinc speciation was calculated from the labile Zn measured by DPASV at different concentrations of added EDTA, which has exchanged with natural ligands for Zn. [Zn−EDTA] is nonlabile and is measured as the difference between initially labile Zn and measured labile Zn after the addition of EDTA. In order to calibrate DPASV sensitivity of labile Zn, we also titrated water samples with standard zinc ion solution. DPASV

TABLE 1. Mean Dissolved (<0.45 μm) Concentrations in the River Glatt and in Groundwater Wells for July 1995 Sampling[a]

parameter	unit	Glatt	GW1	GW2	GW3	GW4	deepGW
no. of samples		39	57	12	12	4	3
pH		8.14	7.46	7.25	7.24	7.2	7.35
temperature	°C	19.8	17.5	11.4	12.5	13.0	11.4
O_2	mg/L	8.7	1.9	6.1	5.5	3.6	7.9
alkalinity	M	4.04×10^{-3}	4.19×10^{-3}	—	5.56×10^{-3}	—	6.02×10^{-3}
Ca	M	1.68×10^{-3}	1.81×10^{-3}	2.44×10^{-3}	2.44×10^{-3}	2.36×10^{-3}	2.79×10^{-3}
Mg	M	6.30×10^{-4}	5.60×10^{-4}	8.11×10^{-4}	7.94×10^{-4}	7.70×10^{-4}	1.00×10^{-3}
Cl	M	6.35×10^{-4}	6.06×10^{-4}	5.95×10^{-4}	5.75×10^{-4}	5.95×10^{-4}	7.11×10^{-4}
Br	M	5.32×10^{-7}	5.53×10^{-7}	4.89×10^{-7}	4.79×10^{-7}	4.98×10^{-7}	5.06×10^{-7}
B	M	1.10×10^{-5}	1.07×10^{-5}	6.66×10^{-6}	7.20×10^{-6}	8.32×10^{-6}	4.55×10^{-6}
Fe	M	3.98×10^{-7}	4.60×10^{-8}	6.80×10^{-8}	5.90×10^{-8}	4.40×10^{-8}	2.59×10^{-8}
Mn	M	3.17×10^{-7}	2.40×10^{-7}	5.10×10^{-9}	3.28×10^{-9}	2.37×10^{-9}	5.80×10^{-9}
Cu	M	4.89×10^{-8}	5.32×10^{-8}	1.73×10^{-8}	1.65×10^{-8}	2.30×10^{-8}	3.93×10^{-8}
Zn	M	8.72×10^{-8}	1.05×10^{-7}	3.30×10^{-8}	2.49×10^{-8}	3.14×10^{-8}	2.86×10^{-8}
Ni	M	2.62×10^{-8}	3.01×10^{-8}	1.14×10^{-8}	1.09×10^{-8}	1.04×10^{-8}	9.40×10^{-9}
Pb	M	1.59×10^{-9}	1.25×10^{-9}	7.24×10^{-10}	4.83×10^{-10}	1.01×10^{-9}	1.88×10^{-10}
Cd	M	8.90×10^{-11}	1.33×10^{-9}	8.90×10^{-11}	3.56×10^{-11}	nd	nd
EDTA	M	4.30×10^{-8}	4.13×10^{-8}	9.36×10^{-9}	1.11×10^{-8}	2.98×10^{-8}	5.6×10^{-9}
Fe−EDTA	M	1.36×10^{-8}	9.04×10^{-9}	2.21×10^{-9}	1.21×10^{-9}	4.64×10^{-9}	—
NTA	M	8.65×10^{-9}	nd	nd	nd	—	—
DOC	mg of C/L	3.35	2.75	1.30	1.15	1.50	0.50

[a] —, not measured; nd, not detected.

measurements of labile Zn were performed with the same apparatus as for DPCSV of Cu determination.

When the samples are titrated with EDTA in the same concentration range as initially labile Zn (10−200 nM), the added EDTA competes with inorganic and labile organic complexes for Zn. Therefore, complexing coefficients of weak (labile) organic complexes are obtained from the measured labile Zn concentration in the presence of EDTA. Using this coefficient, the concentrations of free zinc ions and inorganic and weak organic complexes in original water are evaluated from the mass balance of initially labile Zn. The difference between total dissolved Zn and labile Zn is considered as strong organic complexes. Assuming that Zn competes with Cu for the same strong ligands, we obtained stability constants of Zn complexes with strong ligands based on exchange constants estimated from total dissolved and free ion concentrations of Cu and Zn, and labile Zn concentrations in the same samples (*30*).

Results

Metal Concentrations in the River Glatt and in Groundwater. In Table 1, the changes of the concentrations of the major ions, the metals, and EDTA during infiltration are given. The wells GW2 and GW3 have for all parameters similar concentrations as the deep groundwater and are different from the river and the wells GW1 and GW4. GW1 and GW4 are lying on a direct flow path, while the water of the two other wells seems to consist mainly of deep groundwater. Boron can be used as a tracer for anthropogenic influence, because it is not eliminated during bank filtration of river water (*31*). A dilution factor of metal concentration in the well i can be expressed as a ratio to boron, referred to the river:

$$\text{dilution factor} = \frac{\text{metal}_i}{\text{boron}_i} \bigg/ \frac{\text{metal}_{\text{Glatt}}}{\text{boron}_{\text{Glatt}}} \quad (1)$$

This ratio becomes 1 for all metals in the Glatt. If the ratio is smaller than 1, then the metal has been removed more than boron; if the ratio is higher than 1, then the metal has a source compared to the nonreactive boron. In Figure 2, the ratio is shown for some metals on the direct flow path from the river to GW1 and GW4. Cu, Zn, and Ni are higher in GW1 than in the Glatt and decrease further on (see also Table 1). Ca increases by a factor of nearly 2 from the river to the deep groundwater. Due to our filtration technique, we
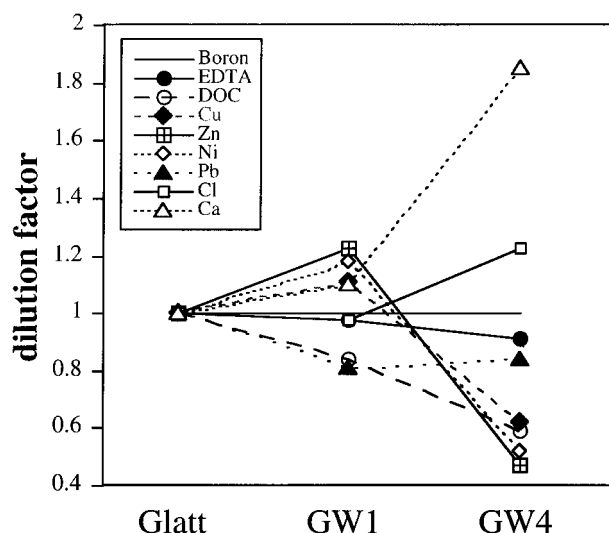

FIGURE 2. Dilution factor of different metals, EDTA, DOC, and chloride compared to boron as tracer for Glatt, GW1, and GW4 according to eq 1. A ratio smaller than 1 shows that the species is better removed from the water than boron; a ration higher than 1 that there is a source for the species.

do not distinguish between truly dissolved and colloidal fractions. The significant decrease of iron from the river to the first well can be due to the removal of colloids during infiltration. Since all samples contain at least 1 mg/L oxygen, no reduction of iron is taking place. The dissolved fraction of other metals like Cu or Zn may be overestimated due to the presence of colloids.

Concentrations of Total EDTA and Fe−EDTA. Total EDTA concentrations varied between 2×10^{-8} and 7×10^{-8} M in the Glatt, which is in the same range as found by Kari and Giger (*7*). Wells GW2 and GW3 have a lower EDTA concentration than GW1 or GW4. If no biodegradation takes place, then this decrease must be due to mixing with deeper water. The geochemical parameters, especially for GW2, support this hypothesis because the water from this well is more like the deep groundwater than the Glatt water. GW4 at 26 m from the river shows again a higher concentration of EDTA. The dilution factor of total EDTA according to eq 1 for GW1 and GW4 is close to 1, indicating that it behaves conservatively (Figure 2).
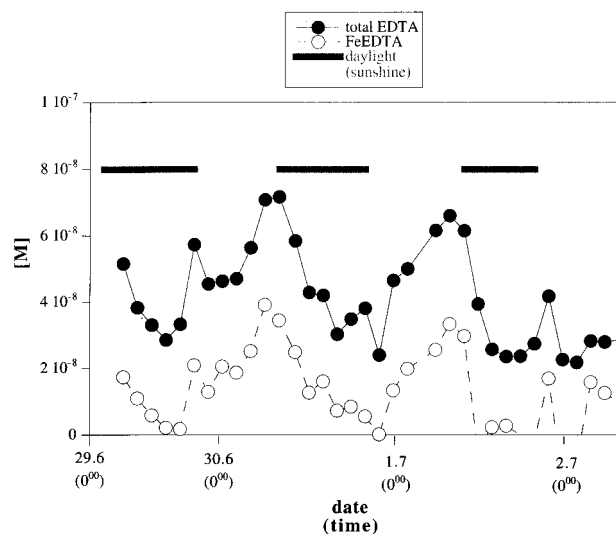
FIGURE 3. Concentration of Fe(III)—EDTA and total EDTA in river Glatt during the July sampling. The samples are 1.5-h composite samples (a sample every 15 min). The bars give the period of clear sky with sunshine.
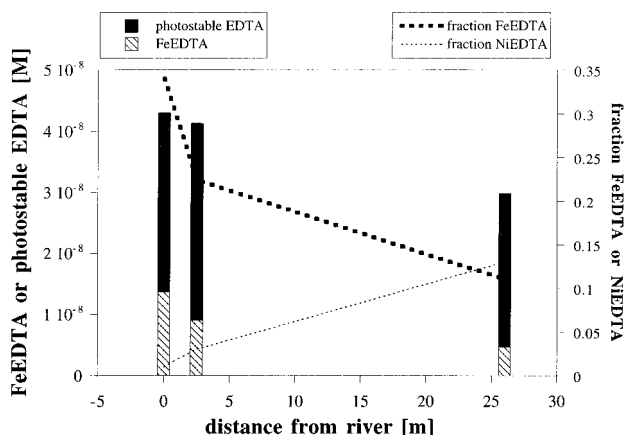

FIGURE 4. Speciation of EDTA in the Glatt and in groundwater GW1 and GW4 from July 1995. Concentration of Fe—EDTA and of photostable EDTA and the fractions of Fe—EDTA and Ni—EDTA are shown. Total EDTA and the photostable EDTA were determined analytically; Ni—EDTA was measured semiquantitatively.

The concentration of total EDTA and Fe—EDTA were determined for all samples of the July sampling. On all three days with clear sky and sunshine the concentration of total EDTA in the river Glatt decreased from morning to evening and increased again during the night (Figure 3). The concentration of Fe—EDTA showed the same dynamics. In the evening no Fe—EDTA was detected. The photostable complexes—the difference between total EDTA and Fe—EDTA—were more or less constant during the sampling period. The decrease in Fe—EDTA can be explained by its photodegradation, according to the short half-life (2 h) under the field conditions (7).

The measured speciation of EDTA for the July sampling is plotted in Figure 4. The fraction of Fe—EDTA decreases from 0.35 in Glatt to about 0.1 in GW4. Fe—EDTA is always much less than total dissolved Fe. Ni—EDTA, semiquantitatively determined, was less than 5—20% in all samples, as shown also in Figure 4.

NTA and DOC. NTA in the river Glatt is much lower (5 $\times$ 10^{-9} M to 2 $\times$ 10^{-8} M) than EDTA (6 $\times$ 10^{-8} M). Biodegradation of NTA is very fast during the summer. From river to the groundwater there is almost a complete degradation of NTA. Schaffner et al. (22) have observed 10 years ago at the same infiltration site the same behavior, but with much
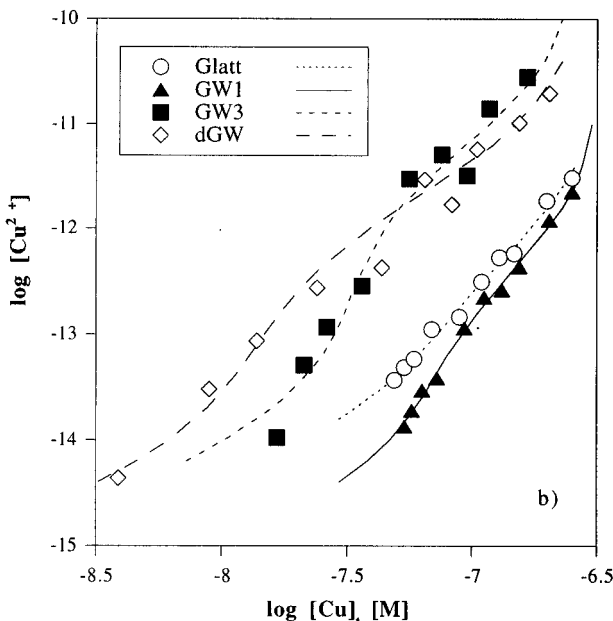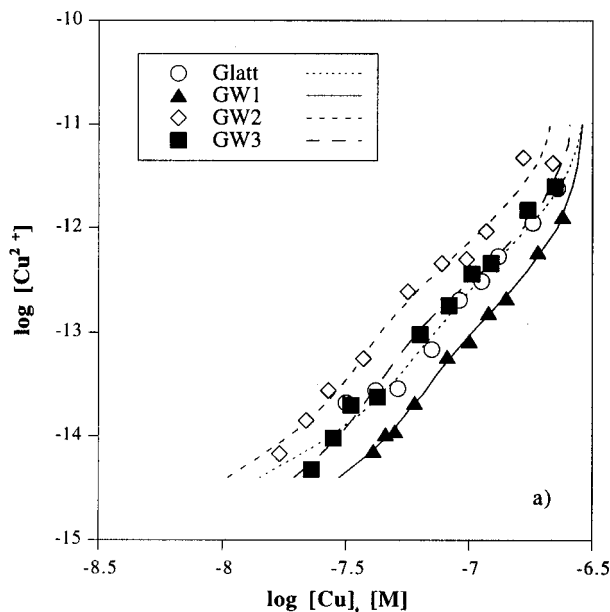

FIGURE 5. (a) Titration of Glatt and groundwaters with Cu and determination of Cu^{2+} in the samples from March 1995. (b) Titration of Glatt and groundwaters with Cu and determination of Cu^{2+} in the samples from July 1995.

higher NTA concentrations (4 $\times$ 10^{-8} to 4 $\times$ 10^{-7} M). They found an elimination of 98% in GW1.

DOC shows a slight degradation from Glatt to GW1 (about 20% decrease). The ratio of DOC to boron decreases from Glatt to GW4, indicating microbial degradation of organic compounds (Figure 2). EDTA accounts for 0.2—0.4% of the DOC.

Speciation of Cu and Zn. Cu titrations of the water samples collected in March and July (Figure 5a,b) show an increase in the complexing capacity from river to well GW1 (shift in the titration curves to the right) and a decrease to the wells GW2, GW3, and the deep groundwater (shift of the titration curves to the left). A shift of the titration curve to the left means that the concentration of free Cu^{2+} is higher at the same total Cu than in the river water. In the March sampling, the complexing capacity of GW2 is weaker than GW3: this finding also indicates that this water has a longer residence time than it would have from a direct flow path.

TABLE 2. Speciation of Cu and Zn at pH 8 in River Water and Groundwater in July As Determined by Ligand Exchange and Voltammetry[a]

species		Glatt	GW1	GW3	deepGW
Cu_{tot}	[M]	4.89×10^{-8}	5.32×10^{-8}	1.65×10^{-8}	3.93×10^{-9}
Zn_{tot}	[M]	8.72×10^{-8}	1.05×10^{-7}	2.49×10^{-8}	2.86×10^{-8}
L1	[M]	1.5×10^{-7}	1.35×10^{-7}	5×10^{-8}	4×10^{-8}
L2	[M]	2.62×10^{-7}	2.54×10^{-7}	2.32×10^{-7}	2.63×10^{-8}
log K CuL1		13.57	14.23	13.65	13.88
log K CuL2		11.79	12.04	10.75	11.03
log K ZnL1		9.80	9.45	9.34	10.04
log K ZnL2		7.80	7.93	7.37	8.15
log K_{cond} Cu−EDTA		17.36			
log K_{cond} Zn−EDTA		15.16			
CuL1	[M]	4.33×10^{-8}	4.94×10^{-8}	1.62×10^{-8}	3.91×10^{-9}
CuL2	[M]	5.57×10^{-9}	3.79×10^{-9}	3.05×10^{-10}	1.52×10^{-11}
pCu		13.43	13.87	13.98	14.36
ZnL1	[M]	8.08×10^{-8}	7.71×10^{-8}	2.27×10^{-8}	2.73×10^{-8}
ZnL2	[M]	6.0×10^{-9}	2.59×10^{-8}	1.56×10^{-9}	7.63×10^{-10}
Zn_{inorg}	[M]	5.9×10^{-10}	1.46×10^{-9}	6.48×10^{-10}	3.18×10^{-10}
pZn		9.44	8.93	9.54	9.68

[a] It is assumed that the same ligands L1 and L2 complex both Cu and Zn. The concentration of L1 was adjusted from the analytically determined CuL1 and ZnL1. The nonlabile Zn as measured by polarography corresponds to ZnL1 + Zn−EDTA. The conditional stability constants of Cu−EDTA and Zn−EDTA at pH 8 are also given.

In the July sampling, the deep groundwater had the lowest complexing capacity.
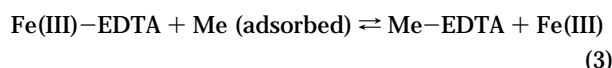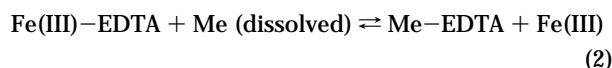
The results of Cu and Zn speciation for the July sampling are shown in Table 2, in which most of the parameters were obtained directly from the determination of the metal speciation. Assuming that Cu and Zn compete for the same strong ligand L1 and the weak ligand L2 and that the nonlabile Zn corresponds to ZnL1 + Zn−EDTA, we can estimate the total concentration of L1 and L2 and adjust the values so that the result of the calculation fits exactly the data from the Zn and Cu titrations. These data are shown in Table 2.

The relative concentration of the strongly complexed Cu (CuL1) to dissolved Cu rises in the series Glatt < GW1 < GW3 < deepGW from 88.5 to 99.5%. The longer the residence time of the groundwater, the more important become the strong complexes, while the weak complexes (CuL2) decrease from 11.4 to 0.4%. The weakly complexed Cu is exchanged against stronger complexes.

Dissolved Zn increases from the river to the first well at a distance of 2.5 m and decreases then to lower levels in GW4 and in the deep groundwater. Most of dissolved Zn in the deep groundwater is in the form of strong complexes ZnL1. The weak Zn complexes ZnL2 increase from 6.6 to 22.7% from Glatt to well GW1 and decrease to 12% in GW3 and to 3.3 in the deep groundwater (Table 2). The Zn that is released during infiltration can form complexes with L2, which is in excess over Cu and Zn (L1 has only a slight excess over Zn and Cu). In GW3 and deepGW with much lower total Zn concentrations, only the strong complexes ZnL1 are important.

Discussion

The speciation of EDTA changes during infiltration. The analytical determination of Fe−EDTA shows that its fraction is decreasing. This can be explained by two possible reaction types:

$$Fe(III)-EDTA + Me \text{ (dissolved)} \rightleftarrows Me-EDTA + Fe(III) \tag{2}$$

$$Fe(III)-EDTA + Me \text{ (adsorbed)} \rightleftarrows Me-EDTA + Fe(III) \tag{3}$$

Fe−EDTA can react in a homogeneous reaction in the interstitial water with free metal ions or weak complexes or in a heterogeneous reaction with adsorbed metals. The half-life of the reaction of Fe−EDTA with Zn (eq 2) was found to be 20 days under conditions of the river Glatt (14). The hydraulic time from river to well GW4 is about 8 days (23). In our field study, the mean value for the fraction of Fe−EDTA was 0.35 in the Glatt and 0.11 in the well GW4. Labile Zn ([ZnL2] + [Zn_{inorg}] + [Zn^{2+}]) was 6.4×10^{-9} M in the Glatt and 2.54×10^{-8} M in GW1. If labile Zn is taken as a steady-state concentration and $10.3 \text{ M}^{-1} \text{ s}^{-1}$ is taken as the kinetic rate constant (14) to estimate Fe−EDTA decrease, then after 8 days it decreases only to 96% of the initial concentration (for the labile Zn of the Glatt) or to 83% (for the higher labile Zn of GW1). In GW3, the labile Zn is much less, and the reaction will become much slower. The measured decrease of Fe−EDTA from Glatt to GW4 is to 49% (mixing included). If Zn is the only metal that reacts with Fe−EDTA in the system, then the decrease could not be completely explained by a homogeneous reaction. The exchange reactions of Pb^{2+} and Ni^{2+} with Fe−EDTA at pH 8 are 8 and 1540 times slower than Zn^{2+} (32). Zn is therefore most likely the metal that Fe−EDTA is reacting with in solution.

The rate constants for the exchange of Fe−EDTA with adsorbed metals have also been determined (32). The reaction with adsorbed Zn^{2+} was found to be in the same range as with dissolved Zn, while the exchange with Ni^{2+} and Pb^{2+} was found to be much faster than in solution. Such heterogeneous exchange reactions with adsorbed metals could account for the fast disappearance of Fe−EDTA.

Davis et al. (2, 3) have studied the behavior of metal−EDTA complexes (Pb−EDTA, Zn−EDTA, Cu−EDTA, and Ni−EDTA) in a sandy aquifer at pH 6. They have observed dissolution reactions leading to Fe(III)−EDTA. Such reactions are favored by the low pH (13). In our field system with a pH between 7.2 and 8, we did not find such dissolution reactions but observed the opposite reactions, this means the exchange of Fe−EDTA against other metals. While in the aquifer of Davis et al. (2, 3) the mobility of the heavy metal was reduced due to the dissolution and the subsequent adsorption of the released metal, we found an indication of a remobilization reaction, exchanging dissolved complexed Fe−EDTA against other metals (presumably Zn or Pb). We can conclude that, at a pH above 7, no dissolution reaction occurs and that Fe−EDTA is exchanging with other metals and remobilizing them.

Is it possible to calculate the concentration of Fe−EDTA, Ni−EDTA, and the other species from the measured con-

TABLE 3. Calculated Speciation of EDTA in a Glatt Sample from July 1996 for Important EDTA Species (in % of Total EDTA)

	1[a]	2[b]
Fe(III)−EDTA	0.01	31.6*
Ni−EDTA	34	6*
Zn−EDTA	24	32
Ca−EDTA	0.05	13
Cu−EDTA	41	0.8
Mn(II)−EDTA	0.1	15
Pb−EDTA	0.2	2

[a] Total concentrations of all metals, EDTA, and NTA. [b] Fe−EDTA fixed at 31.6% of total EDTA; Ni−EDTA fixed at 6% of total EDTA; natural ligands for Cu and Zn included. (*) Fixed as measured.
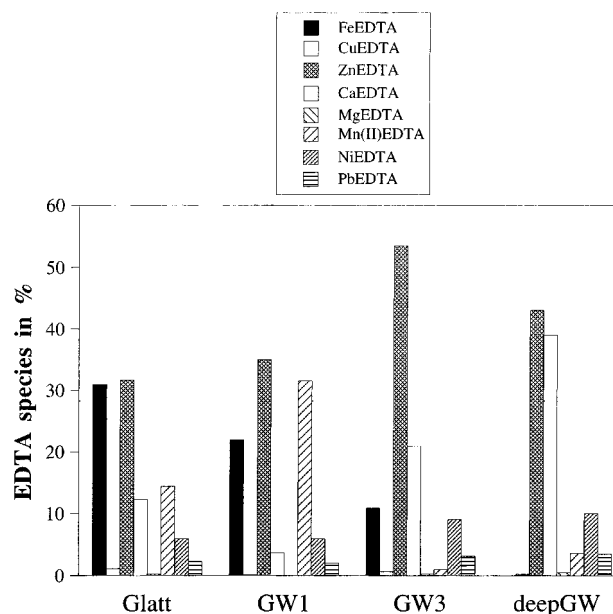

FIGURE 6. Speciation of EDTA in Glatt and groundwater in July 1995 as determined by MICROQL with the constants and concentrations for Cu and Zn ligands (Table 2), EDTA, and inorganic speciation (Table 1).

centrations of EDTA and the metals? We have tried to calculate the speciation of a sample from the river Glatt under two conditions: a simple model using only total concentrations and equilibrium for all species and a more complicated model where the results of the analytically determined speciation of Cu, Zn, and EDTA were included and only partial equilibrium is assumed.

In the first model, we have used only total concentrations of the major ions Ca and Mg; alkalinity; total concentrations of the metals Cu, Zn, Ni, Fe, Mn, and Pb; and total EDTA and NTA. All calculations were done with the speciation program MICROQL (33) based on equilibrium. Under these conditions Cu−EDTA, Zn−EDTA, and Ni−EDTA are the main species while Fe−EDTA is less than 0.1% (Table 3). This is much lower than the measured 31.6%. It is known that Fe−EDTA is not in equilibrium in the river Glatt due to the slow exchange kinetics (14).

For the second calculation, we consider partial equilibrium of EDTA with the metals except Fe and Ni. Therefore we consider only the photostable EDTA (all species but Fe−EDTA) as thermodynamically exchangeable species and fix the value of Fe−EDTA at the determined value (31.6%) and Ni−EDTA at 6%. Ni−EDTA with calculated 34% is also much higher than the analytically determined value of less than 10%. Two possibilities may explain this difference: there are either other strong (natural) ligands for Ni or Ni is not in equilibrium with metal−EDTA complexes due to slow exchange kinetics. The exchange rates of Ni^{2+} with different Me−EDTA complexes at pH 7.2 in homogeneous solution have been determined by Nowack (32). Under the conditions of the Glatt, the half-life of Ni^{2+} with Ca−EDTA is 50 days, with Zn−EDTA it is 13 years, and with Fe−EDTA it is 113 years. It can be, therefore, assumed that Ni^{2+} is not at equilibrium with metal−EDTA species. An equilibrium calculation for both Fe−EDTA and Ni−EDTA is therefore not possible. Natural ligands for Ni have been determined by Donat et al. (34) in South San Francisco Bay with a log K of >17. It is possible that in the river Glatt such ligands are also present. We also improve our model and take into account the natural ligands L1 and L2 for Cu and Zn that we have determined.

The results for the second calculation are also shown in Table 3 for the Glatt River and in Figure 6 for the different groundwater samples. Zn−EDTA turns out to be in all samples the most important EDTA species with a fraction between 40 and 60% of total EDTA. Mn(II)−EDTA becomes very important in GW1 with 40% of total EDTA and in the Glatt with 20%. Mn(II)−EDTA is so abundant because the concentration of Mn(II) in the first groundwater is very high and because Mn(II) is not complexed by natural organic ligands. In GW3 and the deepGW, Mn(II)−EDTA is not important due to the very low concentration of Mn. Ca−EDTA is also a common species with a fraction between 5 and 40%. The highest fraction is found in the deep groundwater where the metal concentrations are low. Pb−EDTA is in all samples about 3%, and Cu−EDTA and Mg−EDTA are

always below 1% of total EDTA. EDTA is under these conditions not an effective ligand for Cu or Zn in relation to the natural ligands. The calculated Cu−EDTA is always less than 0.1% of total Cu in the groundwater samples. Calculated Zn−EDTA is always less than 20% of total Zn. Although Pb−EDTA is not important for the speciation of EDTA, it may be very important for Pb speciation. If no natural ligands are assumed, 93% of Pb is complexed with EDTA in the Glatt and 91% in GW1. This could explain the relatively high mobility of Pb in GW4 where it is hardly removed (Figure 2) despite the very strong adsorption of Pb onto oxides (35).

These two calculations show that the speciation of EDTA and the metals cannot be determined without the knowledge of the natural ligands and of the slow exchange kinetics of some complexes and metals. The simple procedure of only measuring the total concentration of EDTA and the metals does not result in a proper description of the system. Cu−EDTA and Ni−EDTA are overestimated by far by this simple method. If Fe−EDTA, Ni−EDTA, and the natural ligands for Cu and Zn have been determined analytically, then the speciation of EDTA can be calculated accurately, if equilibrium among these complexes is obtained fast. The reactions of Ca−EDTA with Zn or Cu were found to be fast with a half-life of some hours under natural conditions (14, 36). With respect to these species, there should be equilibrium. We also have to address the role of the colloidal metal fraction. Iron does not cause problems because the fraction of Fe−EDTA is measured. As the Cu and Zn speciation is determined by polarography, the stability constants for the natural ligands are apparent constants that also include equilibrium with the colloidal fraction. The dissolved concentrations used in the calculations may be somewhat overestimated due to the occurrence of colloidal species.

Does NTA have an influence on the mobility of metals in groundwater? The calculated speciation of NTA in the Glatt gives 96% Ca−NTA, 3% Mg−NTA, and 0.4% Zn−NTA. The total biodegradation of NTA from the river to the first well therefore does not cause any change in metal concentrations due to the release of the metals during biodegradation, because Ca−NTA is the most important species.

Are the natural ligands for Cu and Zn always important? If less natural ligands are present, EDTA could be a more effective chelator for these metals. Cu ligands L1 were found

in Swiss rivers from 30 to 100 nM and in Swiss (neutral) lakes from 10 to 100 nM (*27*). This is in the same range as found in this investigation (40−150 nM). Cu was always totally complexed by natural ligands. The strong ligands for Zn were found in Swiss lakes and rivers in concentrations of 4−40 nM, binding in all samples about 50% of the Zn (*26, 30*). These strong ligands also include Zn−EDTA, which is therefore always less than 50% of total Zn. The strong ligands for Cu and Zn appear to be not or only slowly biodegradable in the groundwater. Moreover, they do not react with aquifer material and are transported over wide distances. The polarographic method does not give any answer to the nature of these ligands, but their concentration is not directly proportional to the DOC (*27*). It is expected that in groundwater the ligands are mostly material with fulvic acid character.

We can conclude that a combination of experimental methods and of equilibrium calculations is needed to obtain insights into the speciation of EDTA and its effect on heavy metal mobility on an infiltration path. In the case of river Glatt, with a calcareous geochemical background, the speciation of EDTA is controlled by Zn−EDTA, Ca−EDTA, and Fe(III)−EDTA and in some of the groundwaters by Mn(II)−EDTA. EDTA behaves conservatively with respect to its total concentration on the infiltration path in comparison to borate as a tracer, but its speciation changes. The role of Fe(III)−EDTA is of special interest because this species is not at equilibrium with other metals in the river water. On the infiltration path, Fe(III)−EDTA may exchange with adsorbed metals at pH > 7; this reaction appears to be significant under the conditions encountered in the Glatt River and aquifer, where the fraction of Fe(III)−EDTA decreases in the groundwater. At pH > 7, as this is usually the case in calcareous aquifers, remobilization of adsorbed metals by exchange with Fe(III)−EDTA occurs. The mobility of lead and cadmium may be affected by these reactions; also zinc may be transported as Zn−EDTA, which is already present to a large extent in the river. Peaks of very high EDTA concentrations of up to 1 μM were observed in the river Glatt (*7*). As these high EDTA concentrations consisted of Fe−EDTA, significant remobilization of metals occurs in such events. This behavior is in contrast to studies in aquifers at lower pH (*2, 3*) where the exchange reactions occur in the opposite direction, resulting in the dissolution of iron oxides and the formation of Fe(III)−EDTA. The important parameter that determines the impact of EDTA on metal mobilization in aquifers is thus mainly the pH on the infiltration path. At pH below 7, Fe−EDTA is the most stable species and EDTA does not remobilize metals; at pH values above 7, remobilization of adsorbed metals by EDTA occurs.

Acknowledgments

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