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Speciation of Cu and Zn in Drainage Water from Agricultural Soils

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Inputs of copper and zinc from agricultural soils into the aquatic system were investigated in this study, because of their heavy agricultural usage as feed additives and components of fertilizers and fungicides. As the mobility and bioavailability of these metals are affected by their speciation, the lipophilic, colloidal and organic fractions were determined in drainage water from a loamy and a humic soil treated with fungicides or manure. This study therefore investigates the impact of agricultural activity on a natural environment and furthers our understanding of the mobility of metals in agricultural soils and aquatic pollution in rural areas. Marked increases in the total dissolved metal concentrations were observed in the drainage water during rain events with up to 0.3 μM Cu and 0.26 μM Zn depending on the intensity of the rainfall and soil type. The mobile metal fractions were of a small molecular size (<10 kD) and mainly hydrophilic. Lipophilic complexes originating from a dithiocarbamate (DTC) fungicide could not be observed in the drainage water; however, small amounts of lipophilic metal complexes may be of natural origin. Cu was organically complexed to > 99.9% by abundant organic ligands (log K 10.5−11.0). About 50% of dissolved Zn were electrochemically labile, and the other 50% were complexed by strong organic ligands (log K 8.2−8.6). Therefore very little free metal species were found suggesting a low bioavailability of these metals in the drainage water even at elevated metal concentrations.

Introduction

A previous study has indicated that intensive agriculture results not only in increased nutrient but also in elevated copper and zinc loads to the aquatic system (*1*). It is important to understand the transfer and mobility of metals from fertilized soils into the aquatic system in order to investigate the relevance of agriculture to the pollution of water by metals. The general assumption is that the metals undergo complexation or adsorption in the soil and are retained in the topsoil layer, where they may induce phytotoxicity problems. In the past, studies which investigated the mobility of metals in soils were based on sequential extractions of the soil and showed little movement of the metals with the soil profiles over years, provided that the pH of the soil did not decrease (*2−4*). As the analyses were not dynamic, fast movements could not be observed. The present study investigates the mobility of Cu and Zn from fertilized soils in the drainage water and thereby determines the importance of various

factors such as soil type, rain intensity and application of manure and metal containing fungicides. Of foremost concern is the impact of the metals on the water quality.

Recent studies in Switzerland and the UK showed that animal waste contains considerable concentrations of metals (*5, 6*). Especially Cu and Zn are found in high concentrations (mg/L range) in the manure from pigs, cows and hens as these metals are added to the feed in order to improve productivity and for antimicrobial effects. Given that up to 90% of the metals are excreted from the animals (*7*), these metals are enriched in farmyard manure. Solid manure is widely used as organic fertilizer in Europe (*8*). The application of manure on fields often exceeds the uptake by the crops. Therefore the accumulation of metals from manure in soil has been observed in several studies (*5, 9, 10*).

Apart from fertilizers and soil amendments (*11*), pesticides could be a source of metal contamination from agriculture. Fungicides in particular often contain metals. In Swiss biological farming Cu-salts are being used, whereas IP (integrated production) farms are using dithiocarbamates. The synthetic dithiocarbamate ligands (DTC) form lipophilic metal complexes with Zn, Mn, Fe, Na, which have been shown to be rapidly taken up by biota by diffusion across the plasma membrane (*12−14*). The application of DTC may therefore have a disproportionately large impact on aquatic life in an agricultural environment. Dithiocarbamates are thought to have a short half-life in a natural environment (days to months depending on the pH and compartment (*15*)) and have therefore not been given great consideration in previous field studies. However, if the pathway of these organic metal complexes through the soil is faster than previously assumed, they could possibly reach the surface or groundwater before degradation.

Both sources of metals—manure and dithiocarbamate application—were considered in this project to investigate the mobility of Cu and Zn from the soil to the drainage water. Manure and fungicides contain different species of metals, and hence the transport and bioavailability of metals from these two sources may be different. The transport of Cu and Zn from agricultural soils to the drainage water was investigated at two field sites, which differed in their soil type and crop treatment. The concentration and speciation of Cu and Zn were analyzed in the drainage water on an hourly scale during rain events in order to investigate the impact of agricultural activity on the aquatic system. The implications of the speciation for the mobility and bioavailability of Cu and Zn from agricultural soils are discussed. The results obtained in this study are relevant for intensive agricultural regions in the humid continental climate zone.

Experimental Section

Sampling Sites. The two sampling sites were located northeast of Zurich, Switzerland. The sites differed in the type of soils and usage of the fields. The site in Baltenswil contained soil with a humic content of 25% and a pH of 7.3, whereas the site in Lindau contained clayey loam (3% humic content) with a pH of 6.2. The drainage water in Lindau originated from a potato field, of which 0.08 ha were sprayed in the summer of 2001 six times with the fungicide propineb (propylenebis(dithiocarbamate) with 22.6% Zn) in a mixture with 6% Cymoxanil (1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea) and 0.02 ha seven times with a Cu-salt (copper-oxychloride) and no manure was applied that year. This resulted in an estimated annual metal load of 0.24 g Zn/m² and 0.35 g Cu/m² (see Table 1). The drainage system in Baltenswil collected water from grassland (0.085 ha), which

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	applied amount	metal content	sprayed metal amount
manure (1:1 with water)	40 m³/ha	20 mg Zn/L	0.04 g Zn/m²
		5 mg Cu/L	0.01 g Cu/m²
Propineb (70% pure)	2.5 kg/ha	22.6% Zn	0.04 g Zn/m²
$CuCl_2 \times 3Cu(OH)_2$	1.03 kg/ha	50% Cu	0.05 g Cu/m²

was sprayed periodically with ovine manure (estimated annual load: 0.04−0.05 g Cu/m² and 0.16−0.2 g Zn/m²), as well as from a field (0.09 ha), on which potatoes were planted in the year 2000 and maize in 2001. The field was sprayed seven times with propineb in summer 2000 (estimated annual load: 0.28 g Zn/m²) and with atrazine in summer 2001. The drainage pipe systems were at a depth of 0.5−1 m in Baltenswil and 1−2 m in Lindau. Neither field was artificially irrigated. Samples were taken during rain events with an autosampler (ISCO 6700) directly from the drainage pipe every 1−2 h in polypropylene bottles and analyzed for the dissolved metal speciation in summer and autumn 2000 (Baltenswil), summer 2001 (Lindau), autumn 2001 and winter 2002 (Baltenswil). The blank of the autosampler was tested by passing Nanopure water through the device, and no contamination for Cu and Zn was found (<0.15 nM Cu; < 1.5 nM Zn). The meteorological data was obtained from Meteo Swiss and was collected at a station 5 km northwest of the sampling sites.

Analyses. All sampling equipment and bottles were cleaned with 0.1 M HNO₃, and all sample handling was carried out under clean room conditions.

Three soil samples each were taken in February 2002 in Baltenswil and Lindau with a Humax soil sampler down to a depth of 15−20 cm. The samples were dried at 40 °C and sieved over 2 mm. The total metal content was determined by extraction of 10 g soil with 100 mL 2 M HNO₃ for 2 h at 90 °C. The soluble metal fraction was determined by shaking 10 g soil with 25 mL 0.1 M NaNO₃ for 2 h. The filtered extracts were analyzed by ICP−OES (Spectro, power 1200 W).

The drainage water was filtered over 0.45 μm filters (cellulose nitrate or polyethersulfone) and stored at natural pH in a cool room (4 °C) until analyses. Incubation and microscopic analysis of the samples showed that the filtration rendered the samples axenic. The total dissolved metal concentration was analyzed in acidified samples by ICP-MS (PE Elan 5000, power 1150 W) with Rh as internal standard. The ICP-MS techniques were verified by analysis of standardized river water SLRS-3 and SLRS-4 (NRC, Canada). The standard deviations of the ICP-MS measurements were ≤ 5% in the upper concentration range (15−700 nM) and ≤ 10% between 1.5 and 15 nM. DOC (Dissolved Organic Carbon) was measured by high-temperature combustion on an Elementar High TOC II. The pH was measured in the field with a combined glass electrode pH-meter (WTW pH 323 A).

The lipophilic metal fraction was determined by fractionation over a C18 column (Bakerbond SPE). The column was activated and cleaned with MeOH, HNO₃ (pH 3) and Nanopure water (resistance 18.3 MΩ, DOC: 0.1−0.2 mg/L). 250−500 mL of the sample were passed over the column with a flow rate of 7−10 mL/min, to achieve a quantifiable Cu and Zn signal in the ICP-MS analysis of the eluents. The column was rinsed with 100 mL of Nanopure water prior to elution with 2−3 × 2 mL of 60% methanol in Nanopure water followed by 2−3 × 2 mL of HNO₃ (pH 3). The technique was verified by applying the same amounts of Zn (30 μg and 300 μg) on the column using propineb, an inorganic Zn-standard (zinc nitrate in 2% nitric acid) and ZnEDTA solutions. ZnEDTA was not adsorbed on the column, and the Zn concentration

was in both eluates comparable to the blank. Hydrophilic organic complexes are therefore not retained by this column. Part of the free and inorganic Zn can adsorb on the uncapped silanol groups of the column. In the eluates from the Zn-standard Zn was detected in the acidic fraction, but none was detected in the methanol fraction. Zn−Propineb was adsorbed on the column and found in the 60% methanol fraction and in the acidic eluate. Methanol therefore elutes organic lipophilic metal complexes, whereas the acid elutes free or inorganic metal species. The technique is not quantitative as the last elution did not remove all of the adsorbed metal from the column. However, the percent recovery should be the same in all samples as the volume of the sample, type of sample and eluate as well as the flow rate and quantity of adsorbent was comparable. Therefore the technique should allow an observation in the change of speciation by comparing the proportions of eluted and total dissolved metal. The eluates were analyzed by ICP-MS using a flow injection system (FIAS 400) for the sample introduction with a sampling loop of 200 μL. The standard deviation of the technique was tested on two different days by applying 1 μg Zn−Propineb on two, respectively three C18 columns, elution with 2 × 2 mL of 60% methanol and FIAS−ICP-MS analysis and was found to be below 10%.

The organic metal speciation of Cu was analyzed in the 0.45 μm filtered samples by titration with added Cu (31.5−944 nM) using 1 mM catechol as an added ligand. The adsorbed complexes were determined by cathodic stripping voltammetry according to Xue and Sigg (*16*). The pH was adjusted to the natural pH (6.9−7.2) with a gas mixture of 3−5% CO₂ in N₂ (Carbagas), and no buffer was added to the samples. The Cu standard was left to equilibrate in the samples overnight and catechol was added the next day. It was found that an equilibration time of 5 min was not sufficient for the equilibration of the added ligand with the natural Cu species in these samples. A system was therefore developed which allowed the simultaneous purging of 10 darkened voltammetric cells with the gas mixture for 3−5 h after which the added ligand was equilibrated. The organic speciation of Zn was determined by anodic stripping voltammetry, and the free Zn concentration was determined by equilibration with 20−40 nM EDTA (*17*). A 757 VA Computrace voltammetric stand from Metrohm with a hanging mercury drop electrode (HMDE), a Ag/AgCl reference electrode and a Pt-counter electrode was used for all voltammetric measurements. The gas mixture was also used for the voltammetric measurement of Cu and Zn. After calculation of the free metal concentration (*16, 17*), the conditional stability constants and concentrations of the natural ligand were determined using the FITEQL 4.0 program (*18*). Two ligands (L₁ and L₂) can be determined for Cu. For Zn only the conditional stability constant of the weaker ligand L₂ can be determined. The stability constants for inorganic complexes and complexes with catechol and EDTA were taken from reference data (*19*) and corrected with the Davies equation for the ionic strength. The conditional stability constant log K is only valid in the concentration range and at the pH used in the experiments.

The colloidal fraction is defined as submicron particles which have a diameter < 0.45 μm and a molecular weight > 10 kD and was determined after Wen et al. (*20*). The sample (<0.45 μm) was filtered with a cross-flow ultrafiltration (Filtron and Watson Marlor 701 S) equipped with two 10 kD low protein binding modified polyethersulfone membranes (Omega, 5 SQ Feet Filtron). The colloidal retentate was concentrated by a factor of 4.2−11 relative to the original sample. The flow rate of the ultrafiltrate was 22 mL/min.

TABLE 2. Total and Soluble Cu and Zn Contents in the Soils (Per g Dry Weight)

sampling site	Cu total[a] μg/g	Cu soluble[b] μg/g	Zn total[a] μg/g	Zn soluble[b] μg/g
Lindau	48	0.05	82	0.2
Baltenswil	78	0.2	284	0.3
Swiss guideline values	40	0.7	150	0.5

[a] Extraction with 2 M HNO_3. [b] Extraction with 0.1 M $NaNO_3$.

TABLE 3. Average Concentrations of Cu, Zn and DOC in the Drainage System

sampling site	Cu nM	Zn nM	DOC mg/L
Under Dry Weather Conditions			
Lindau	24	5	2
Baltenswil	27	6	6
Maximal Concentrations during Rain Events			
Lindau	297	258	8
Baltenswil	175	95	15

Results

Concentrations of Cu and Zn in the Soils. The Cu and Zn contents of the soils are summarized in Table 2. The humic soil in Baltenswil twice exceeded the Swiss guideline values for pollutants in soil (*21*) for the total Cu and Zn content. The clayey loam in Lindau showed lower Cu and Zn contents, but the total Cu concentrations (48 μg/g) also exceeded the guideline value (40 μg/g).

Concentrations of Cu and Zn in the Drainage Water. The average metal concentrations under dry and wet weather conditions are summarized in Table 3. The dissolved Cu concentrations in the drainage water of both soils were during dry periods 24−27 nM. During rain events the concentrations increased approximately 10-fold to 297 nM in Lindau and 175 nM in Baltenswil. Under dry weather conditions the dissolved Zn concentrations in the drainage were around 5 nM. As with Cu the concentrations increased depending on the intensity and duration of the rainfall up to 258 nM in Lindau and 95 nM in Baltenswil.

The influence of the intensity and duration of the rainfall on the mobility of metals was especially apparent in Lindau. A long lasting rain event (Figure 1B) led to an obvious increase in metal concentrations in the drainage water, whereas a severe but short rainfall resulted only in a minimal increase (Figure 1A).

The impact of the manure application was analyzed at different periods in Baltenswil: in the summer and in November 2000 (Figure 2), in October 2001 (Figure 3) and February 2002 (data not shown). Rainfall one week (Figure 2A) or five weeks (Figure 3) after the application of manure led to a marked increase in the dissolved Cu and Zn concentrations in the drainage. After the end of the agricultural activity in November 2000 (four months after the last application of manure) and February 2002, no increased Cu and Zn concentrations could be measured during a week long rain event (Figure 2B). The metal concentrations during these periods were about 40 ± 6 nM Cu and 17 ± 4 nM Zn.

No variation in the pH was observed in the present study as the pH of the drainage water was always close to pH 7. However, during rain events the concentrations of the total dissolved Cu and to a lesser extent of the Zn increased together with the DOC (Figure 4), suggesting a correlation between the organic content of the soil solution and the mobility of these metals in the soil. However, no correlation was found between DOC and the ligand concentration,
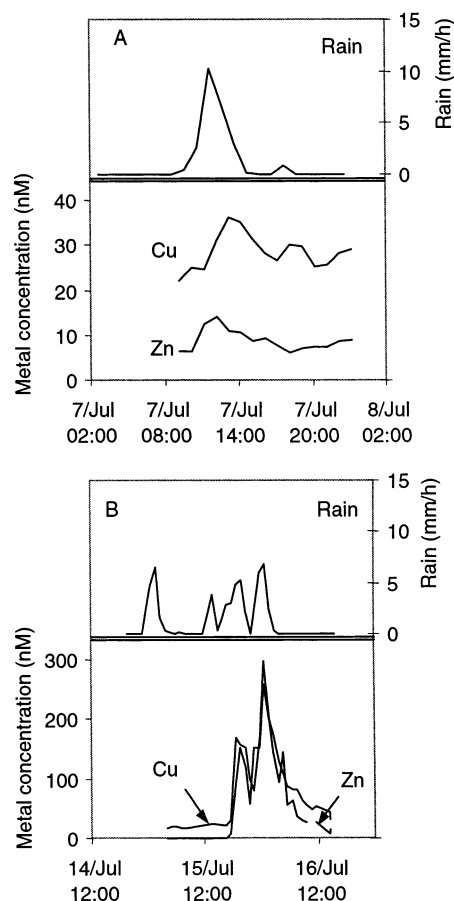

FIGURE 1. Total dissolved Cu and Zn concentrations (nM) in the drainage system in Lindau in July 2001 (A: 7−8 July; B: 14−17 July) during two rain events. The amount of rainfall (mm/h) is illustrated in the upper graphs.

indicating that these organic compounds have (at least partly) a different source.

Based on the amount of rainfall (assuming that 30% evaporates) the Cu and Zn load during a rain event can be estimated and compared to the applied amount. This estimation revealed that during the first rainfall after the application of manure and fungicide in Baltenswil (Figure 2 A) ∼2% of the applied Cu and ∼0.13% of the applied Zn can be found in the drainage water. Five weeks after the application of manure (Figure 3) the amount washed out in comparison to the applied amount is ∼1.3% for Cu and ∼0.1% for Zn. In Lindau ∼3% of the applied Cu and ∼0.8% of the applied Zn were found in the drainage water during a long lasting rain event (Figure 1B), whereas ∼0.3% of Cu and ∼0.03% of Zn were found during a short, but severe rainfall (Figure 1A).

Speciation of Cu and Zn. The lipophilic fraction of the metal species is an indirect measurement of the metal species originating from the dithiocarbamate. Expressed in percent of the total dissolved metal content, this figure could indicate a disproportionately large impact of the dithiocarbamate-complexes to the biota in the aquatic system. The percentage of lipophilic Cu and Zn of the total dissolved metal concentration in relation to the rain data is presented in Figure 5A for Lindau and Figure 5B for Baltenswil. Apart from two exceptions 4−8% of the dissolved Cu complexes and less than 0.5% of the dissolved Zn complexes were lipophilic during the whole sampling period in Lindau. A slight increase in the lipophilic fraction was observed in Baltenswil in relation to the rainfall. During a long lasting rain event the lipophilic Cu fraction increased from ∼2%
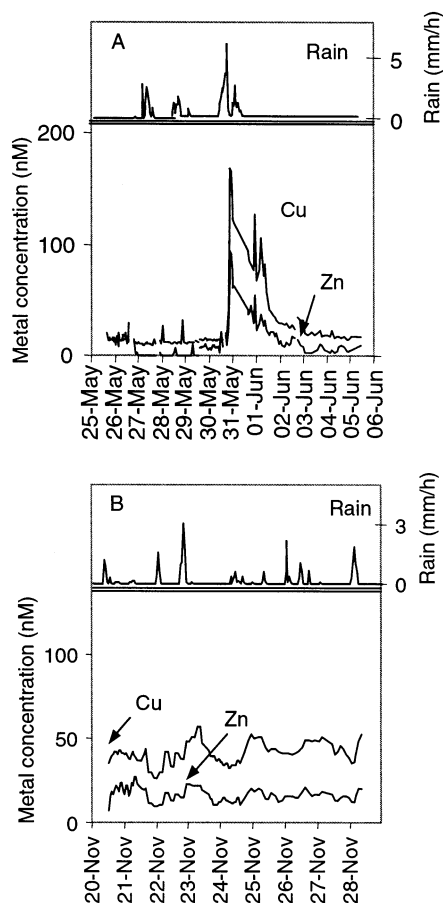
FIGURE 2. The impact of the manure application on the total dissolved Cu and Zn concentrations (nM) in the drainage system in Baltenswil in May/June (A) and November (B) 2000. Manure was applied on May 25. The amount of rainfall (mm/h) is illustrated in the upper graphs.
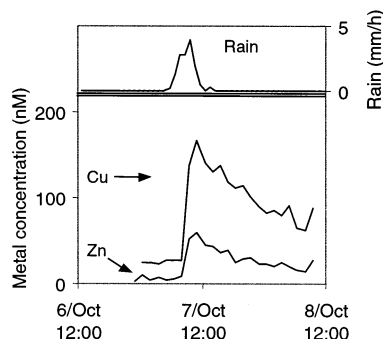

FIGURE 3. The rapid increase of total dissolved Cu and Zn concentrations (nM) in the drainage system in Baltenswil within hours after the onset of rainfall in October 2001. The amount of rainfall (mm/h) is illustrated in the upper graph on the same time scale.

(7/10/2001) to ~8% (25/10/2001) and the lipophilic Zn fraction from ~1% (7/10/2001) to ~3% (25/10/2001).

For Cu as well as for Zn, the colloidal fraction increased together with increasing rainfall on both soils (Figure 6A and B). In Lindau the colloidal fraction reached nearly 7% of the total dissolved Cu (16/7/2001) and in Baltenswil this fraction increased from 1% before a rain event to ~20% during the long lasting rain event (24−25/10/2001). The colloidal Zn fraction was 3−6% in Lindau and increased from 5% to ~20% in Baltenswil.

The organic speciation did not show any significant temporal or soil-type dependent variations as the standard
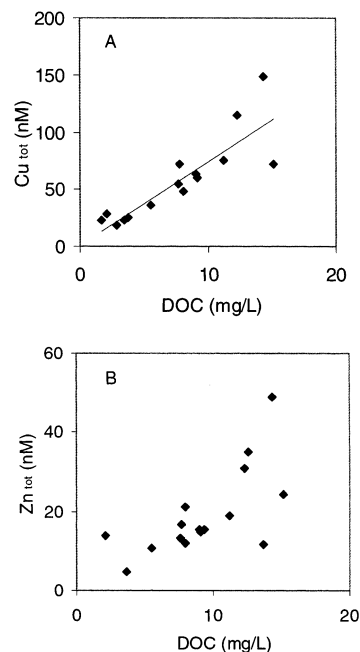

FIGURE 4. Total dissolved Cu (A) and Zn (B) concentrations (nM) in the drainage systems in relation to the DOC concentration (mg/L). The line in graph A illustrates the linear regression of the data ($[Cu]_{tot} = 7 \times 10^{-9} \times [DOC] + 8 \times 10^{-10}$; $r^2 = 0.7624$).
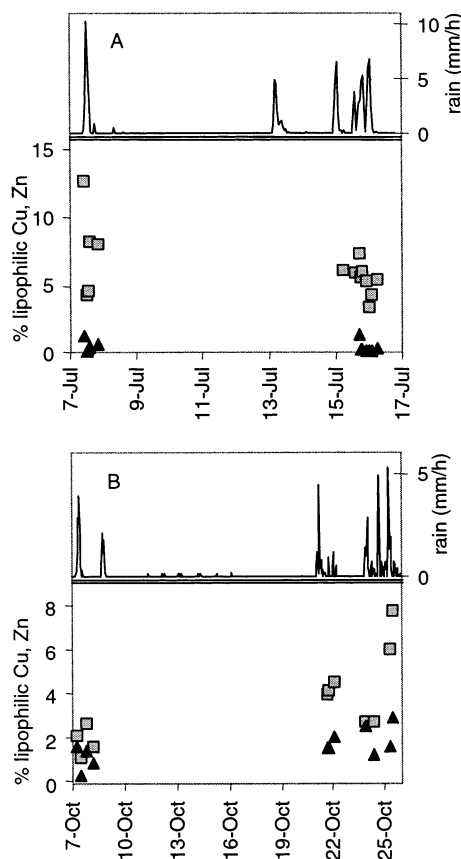

FIGURE 5. Percentage of lipophilic Cu (grey squares) and Zn (black triangles) of the total dissolved concentrations in relation to the amount of rain (mm/h) (top graph) in Lindau (A) and Baltenswil (B) in 2001.

deviation was within the 10% error and is summarized in Table 4. Both metals were predominately organically complexed in the mobile fraction. The Cu species varied
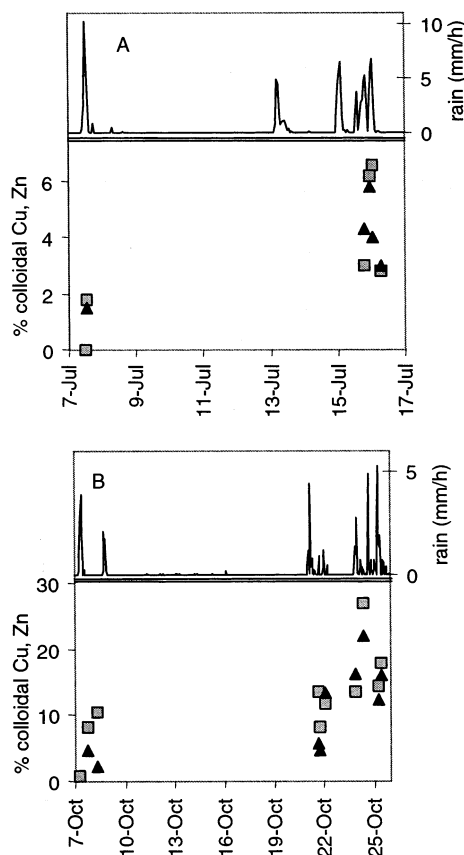
FIGURE 6. Percentage of colloidal Cu (grey squares) and Zn (black triangles) of the total dissolved concentrations in relation to the amount of rain (mm/h) (top graph) in Lindau (A) and Baltenswil (B) in 2001.

proportionally to the total dissolved Cu concentration and over 99.9% of the dissolved Cu was organically bound. Therefore, as the total dissolved Cu concentration increased by an order of magnitude, the stability constant of the organic Cu complexes decreased by the same order and the ligand concentration doubled. The negative logarithm of the free Cu concentration pCu was 11.6−11.8 (±0.9) at the two sites. In average, 50% of Zn in the drainage water were electrochemically labile (free, inorganic and weakly organically complexed Zn), and the other 50% were strongly organically complexed. With increasing Zn concentrations, the strong Zn complexes increased ($[ZnL_1] = 0.8 \times [Zn]_{tot} + 7 \times 10^{-9}$, $r^2 = 0.8644$), whereas during a dry period 60−100% of the total dissolved Zn were labile.

Discussion

Metal Release into Drainage Water in Function of Soil Type, Intensity of Rain Fall and Manure Application. Organic and loamy soils have a great sorption capacity for metals which explains the high metal concentrations in the soils (Table 2). Because of the high sorption capacity of these soils for metals, no groundwater hazard is generally expected. However, the investigation of the metal concentrations in the drainage water during rain events revealed an interesting process. The dissolved metal concentration of Cu and Zn increased rapidly during a rain event and decreased again after the rain event, which indicated a variable and rapid transport of these metals through the soil within 1 h after the onset of rain (Figure 3). This rapid increase suggests the transport of the metals through preferential flow paths such as worm dwellings, cracks or root channels. This process has been studied in more detail by Bundt et al. (*22*) where it was observed that the concentration of radionuclides was higher in the pref-

erential flow paths and the transport more rapid than in the matrix of the soil.

The increase in the dissolved Cu and Zn concentrations depended on the intensity and duration of the rainfall (Figure 1) and thus on the percolation of the precipitation through the soil. Loamy soil, in particular, has a weak water permeability (*23*), which explains why increased metal concentrations in the drainage water in Lindau were only observed during a long lasting rain event.

The mobility of metals in soil can be increased by a decreasing pH or by an increase in the organic content in the soil solution. It is well-known that at pH values above 6−7 soluble metal organic complexes are being formed with Cu and Zn. The application of manure led to increased metal and DOC concentrations in the drainage water for a period of weeks or months (depending on the amount of rainfall), whereas only slight variations due to the elution of the adsorbed metals in the soil were observed in the winter (Figures 2 and 4). The adsorption of the metals in the soil is reduced by organic complexation, which explains the marked increases in the total dissolved metal concentrations in conjunction with the application of manure and the observation that the mobile Cu and Zn species were mostly organically complexed. An increased solubility of Cu and Zn due to increased organic carbon in amended soils has been observed especially in sandy soils with an elevated metal content (*24−26*).

Despite elevated Zn concentrations in the soil relative to Cu (especially in Baltenswil), the concentration of Zn in the drainage water was consistently lower than that of Cu (Tables 2 and 3). This low concentration can be explained by the low mobility of Zn at pH 7 due to the weak stability of organic Zn complexes and due to the sorption of Zn on oxides and aluminum silicates (*27*). In accordance, the greater elution of Zn in Lindau can be attributed to the lower soil pH of 6.2.

Speciation and Bioavailability. Among other things, the bioavailability of Cu and Zn is related to the lipophilicity of the metal species as well as to their size and organic complexation. The differences in the lipophilic fraction in Lindau were too minor to observe an increase during a rain event and a rapid elution of the dithiocarbamate (Figure 5A). A strong adsorption or inclusion in the organic matter of the soil could possibly prohibit the translocation or elution of the fungicide (*28*). At the time of the application of the DTC as a Zn complex, a Cu-salt was applied on the adjoining field. The DTC forms stronger complexes with Cu than with Zn and is stabilized that way (*29*). It is therefore not surprising that a greater amount of lipophilic Cu-complexes was found even though the Zn-complex was applied on the field. The lipophilic Zn fraction was greater in Baltenswil than in Lindau, even though no dithiocarbamate was sprayed that year (Figure 5B). Lipophilic metal complexes may therefore also be of natural origin.

The assumption that the dithiocarbamate could have a disproportionately strong impact on organisms in the aquatic system due to the formation of lipophilic metal complexes, as suggested by Phinney and Bruland (*12−14*), could not be proven in this study. Only a small fraction of the mobile metal species was lipophilic, and the majority of the species were hydrophilic organic complexes. Such hydrophilic complexes could be degradation products of organic matter, such as fulvic and humic acids. The presence of lipophilic organic metal complexes in natural waters has not yet been investigated in details but could include natural ligands such as catechol.

Colloidal metal species are not as readily bioavailable as dissolved (<10 kD) species. The majority of the mobile metals were, however, small complexes analyzed in the dissolved fraction. During the rain event the colloidal fraction increased (Figure 6). The colloidal fraction in the humic soil was greater

TABLE 4. Average [Cu^{2+}], [Zn^{2+}] and Complexation Parameters Calculated by FITEQL 4.0 in the Drainage Water in Lindau and Baltenswil at pH 6.9–7.2[a]

	n	pCu	Log K_{CuL}	[L]$_{Cu}$ μM	n	pZn	Log K_{ZnL2}	[L$_2$]$_{Zn}$ nM
Lindau	4	11.6 ± 0.9	11.0 ± 0.8	0.2 ± 0.1	6	8.7 ± 0.6	8.2 ± 0.4	30 ± 24
Baltenswil	15	11.8 ± 0.8	10.5 ± 0.5	1.2 ± 0.5	18	8.8 ± 0.5	8.6 ± 0.6	20 ± 16

[a] n = number of samples; pCu = −log [Cu^{2+}], pZn = −log [Zn^{2+}].

than in the loamy soil, which can most likely be attributed to the humic substances. The percentages of colloidal fractions were similar to the average values observed in the Swiss river Thur, which is impacted by inputs from sewage and agricultural runoffs (30), even though lower DOC values were measured in the Thur (1−3 mg/L).

The bioavailability of many metals such as Cu and Zn is mainly dependent on the free metal species according to the FIAM-model (31). However, studies of different soils and soil solutions have shown that Cu is mainly organically complexed. The speciation of Zn in soil solutions is more variable as Zn is readily adsorbed by mineral and organic substances in the soil (32). These observations were confirmed in the present study. The conditional stability constant log K for organic Cu-complexes (log K_{CuL} = 10.5−11.0) was comparable to constants found in freshwater with a pH around 7 (33). The concentration of the ligand originating from the humic soil in Baltenswil ([L]$_{Cu}$ = 1.2 ± 0.5 μM) was however 1−2 orders of magnitude greater than previously reported, whereas the concentrations from the loamy soil in Lindau ([L]$_{Cu}$ = 0.2 ± 0.1 μM) were at the top end previously found. Unlike in most other freshwater systems no second Cu ligand could be found (16, 33). The abundance of the weak ligand may have concealed the presence of a second stronger ligand. Cu therefore seemed to have been complexed by the same type of ligand throughout the investigation, whereby the concentration increased together with the total Cu concentration. The conditional stability constant as well as the ligand concentrations of the weak organic Zn complexes (log K_{ZnL2} = 8.2−8.6, [L$_2$]$_{Zn}$ = 20−30 nM) were comparable to those previously found in freshwater at a pH range of 7.7−8.5 (34). These stability constants do not suggest the presence of dithiocarbamate complexes as they are weaker than the stability constants for different DTC complexes with Zn (log β_2 10 to 13) determined by solvent extraction and polarographic methods (35). No stability constants for Cu-DTC complexes could be found in the literature, but they can be expected to be greater than for Zn.

The analysis of the speciation permits a better description of the significance of the high dissolved metal concentrations during a rain event. Even though the total dissolved fractions increased by an order of magnitude (Table 3), no increase in bioavailable species was observed based on chemical analysis (size fractionation, lipophilicity, organic complexation). No obvious difference between the two metal sources—fungicides and manure—with regards to the metal mobility and speciation was observed, even though slight differences due to the soil type were observed with regards to the amount of lipophilic and colloidal metal species as well as organic Cu ligands.

Relevance of Findings to Surface Waters. The input of Cu and Zn from manure, copperoxychloride and the DTC fungicide (propineb) to agricultural fields per application is comparable (Table 1). Granted that propineb was sprayed six times and an average rain fall of 250 mm in the application time from mid June till mid August (assuming that 30% evaporated) ~1.4 mg Zn/L could reach the drainage water if no metal was adsorbed in the soil. This indicates that in comparison to the dissolved Zn concentrations measured in the drainage water the majority of Zn was adsorbed in the soil and only ~0.1−1% reached the drainage water. If these

estimates are done for one rain event on the studied fields ~2−3% of the applied Cu and < 1% of the applied Zn can be found in the drainage water. These rough estimations support the characterization of these soils as soils with a high sorption capacity for metals and agree with previous reports. The balance and long-term behavior of metals was assessed in pig slurry amended soils over eight years and showed that 0.05% Cu and 0.6% Zn of the applied metals were found in the drainage water of a freely draining sandy silt loam (36).

The concentrations of Cu in the drainage water during dry weather conditions were comparable to the Cu concentrations in Swiss surface waters (33, 37). However, during rain events a 10-fold increase was observed. For Zn the concentrations under dry weather conditions were below the average Zn concentrations found in Swiss surface waters and increased during rain events to concentrations normally found in surface waters. Especially the potentially toxicological effects of Cu should therefore be further investigated in intensive agricultural areas to avoid an endangerment of the aquatic system. The transport through preferential flow paths can lead to short-term, but ecological significant increases in dissolved metal concentrations in the aquatic system.

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