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Measuring Free Metal Ion Concentrations in Situ in Natural Waters Using the Donnan Membrane Technique

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Metal toxicity is not related to the total but rather to the free or labile metal ion concentration. One of the techniques that can be used to measure several free metal ion concentrations simultaneously is the Donnan Membrane Technique (DMT) in combination with the inductively coupled plasma-mass spectrometer (ICP-MS). However, free metal ion concentrations in natural waters are commonly below the detection limit of ICP-MS. We decreased the detection limit by making use of a ligand, and we developed a field DMT cell that can be applied in situ in natural waters. A kinetic approach can be used to calculate free metal ion concentrations when the equilibrium time becomes too large. The field DMT measured in situ in natural waters a free metal ion concentration ranging from 0.015% (Cu) to 13% (Zn) of a total metal concentration ranging from 0.06 nM (Cd) to 237 nM (Zn). The free metal ion concentrations were difficult to predict using an equilibrium speciation model, probably due to the uncertainty in the nature of the dissolved organic matter or the presence of other reactive colloids. It is shown that DMT can follow changes in the free metal ion concentration on times scales less than a day under certain conditions.

Introduction

Pollution of surface waters has led to strict regulations on maximum metal concentrations allowed in natural waters. However, it is often found that the uptake of heavy metals by organisms does not depend only on the total metal concentrations in solution. Instead, better correlations have been found between metal uptake and free metal ion concentrations (1) or labile metal concentrations (2). Even though there are some exceptions (3, 4), the free metal ion concentration is, in most cases, the key factor in predicting bioavailability.

There are two ways to determine the free metal ion concentration: modeling from measurements of total concentrations and measuring directly. However, to model chemical speciation in natural waters is complicated because the nature of the complexing agents and their concentrations is unknown. When the total organic carbon content of the water has been measured, part of this total carbon is often assumed to behave like humic acid, part of it like fulvic acid,

and part of it as inert for metal ion binding. Semimechanistic ion binding models have been developed that can calculate the free metal ion concentrations (e.g., Model VI (5); NICA–Donnan (6); and the multi-surface model (7)) in the presence of humic substances. For certain metals (e.g., Cu^{2+}), these models predict highly variable free metal ion concentrations when assumptions about the composition of the organic matter are varied. So, if these models are used, for example, in risk assessment of metal toxicity, estimation of the free metal ion concentrations may be quite uncertain. Therefore, those models have to be tested by comparing the predicted results with measured values.

Most of the techniques that measure metal speciation can distinguish between free + labile and inert fractions of metals, like stripping chronopotentiometry (SCP; ref 8), diffusive gradients in thin films (DGT; ref 9), and gel-integrated microelectrodes (GIME; ref 10). Even though measuring labile complexes in natural waters can be very useful, it cannot fulfill the need for measuring free metal ion concentrations, which play a key role in both biouptake and chemical modeling of aquatic systems. Ion-selective electrodes (ISE) are restricted to situations when the total dissolved metal concentration is above 1 μM . Cathodic stripping voltammetry (CSV) and phase separation (e.g., resin technique) can have problems with competition effects and equilibrium shifts. A promising technique to measure free metal ion concentrations is the permeation liquid membrane technique (PLM; ref 11), but its applicability depends on the metal binding characteristics of the transport ligand. The gellyfish (12) and the absence of gradients and Nernstian equilibrium stripping (AGNES; ref 13) have not yet been calibrated for multicomponent systems or for low metal ion concentrations.

Another method that can measure free metal ion concentrations is the Donnan Membrane Technique (DMT) which makes use of a cation exchange membrane and is based on the principle of the Donnan membrane equilibrium (14, 15). However, in DMT, peristaltic pumps pump both the donor and the acceptor solution through both compartments of the cell. To use this technique in the field would imply that natural waters could only be measured at the shore, due to the demand for electricity and for a firm base for the pumps and cells. Therefore, the technique has been modified for field applications. In the so-called field DMT, only one chamber with two membranes on both sides is used without any pumping.

The main objective of this study is to compare model calculations on free metal ion concentrations in natural water with field measurements of free metal ion concentrations. To apply the Donnan Membrane Technique to natural waters, the detection limit of the field DMT has to decrease. Therefore, an ion complexing ligand was added to the acceptor solution. In situ DMT measurements were compared to modeled values. In a situation where the equilibrium cannot be reached within several days, a kinetic approach can be used to measure free metal ion concentrations by means of modeling the ion transport across the membrane (16).

Experimental Procedures

To do measurements on natural water systems, one can choose to take water samples into the laboratory or to measure in situ. Bringing samples to the laboratory may lead to contamination problems. Moreover, metal speciation in the samples may change as a consequence of temperature change or bacterial activity, which is important when metal speciation is studied. Therefore, it was decided to use the

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DMT in situ to measure free metal ion concentrations in natural water systems.

DMT Cell. The so-called field DMT cell was modified from another DMT cell that is used to measure in situ speciation in slurry manure (see Figure S1, Supporting Information; ref 17). The lab DMT cell (15) consists of two chambers, a donor and an acceptor chamber. The field DMT cell has only one chamber (the acceptor), on two sides separated from the sample solution (the donor) by cation exchange membranes. It has a volume of approximately 12 mL (in the lab DMT usually an acceptor volume of 15 mL is used), and the surface area of the two membranes is approximately 19 cm² (the lab cell has a surface area of about 7 cm²). The higher surface-to-volume ratio of the field DMT as compared to the lab DMT should lead to a faster cation exchange between the sample (donor) and the acceptor solution (16).

Before the cation exchange membranes are fixed into the DMT cell, they are cleaned and saturated with calcium. Therefore, the membranes are washed several times with 0.1 M HNO₃ to remove metals. Then, after washing with ultrapure water (UPW), the membranes are washed in 1 M Ca(NO₃)₂ to saturate them with calcium. The release of protons by the membrane is compensated by adding NaOH to the Ca(NO₃)₂ solution. After saturating with Ca, the membranes are washed with UPW and then with a Ca(NO₃)₂ solution of the same molarity as used in the acceptor side during the DMT measurements.

When the field cells are used in the lab experiments, the cells were immersed into the sample solution, which was stirred continuously. For in situ measurements, the field DMT is immersed into the river or lake and cation exchange between donor and acceptor takes place without pumping. The natural movement of the water in the river or the lake provides mixing, and a diffusion layer will develop close to the surface of the cell. After retrieval of the DMT cell, the acceptor solution is sucked out of the cell and stored for further analysis. By measuring a cation X that does not form complexes with the ligands present, a correction can be made when there is a salt difference between donor and acceptor (15).

Decreasing the Detection Limit of the DMT. To be able to measure free metal ion concentrations when these concentrations are below the detection limit of the ICP-MS, we have chosen to add a metal-complexing ligand to the acceptor solution. By complexation with the ligand, the total metal concentration in the acceptor solution can be raised above the detection limit of the ICP-MS. Synthetic ligands, like EDTA and NTA, and natural ligands, like humic acid and fulvic acid, can be used to lower the detection limit of the DMT, but most synthetic ligands have the problem of being very sensitive in a small concentration range. Because of only a single or only a few different binding sites, metal complexation may change drastically within a small concentration range. Therefore, a purified humic acid with a large range of well-known metal binding characteristics (19) has been used for this study. The metal binding by humic acid is similar to the metal binding by natural organic matter. Therefore, metal ions whose activity is strongly decreased by natural organic matter are automatically highly complexed by humic acid in the acceptor side. By means of the NICA–Donnan model (6), the free metal ion concentration in the acceptor at equilibrium is calculated based on the known model parameters and measured total metal concentrations in the acceptor solution.

Before the cation exchange begins, the total metal concentration in the acceptor solution is usually below the detection limit when no ligands are added to the acceptor side. However, when natural ligands are added to the acceptor side, residual metal concentrations of the ligands may contribute to the total metal concentration in the acceptor

measured at the end of the experiment in case of the kinetic interpretation of the data. For the humic acid used in this study, residual metal concentrations range from 0.56 nM for Pb to 87 nM for Zn (see Table S1, Supporting Information). For equilibrium speciation calculations, it is assumed that the metal ions in the residue bind reversibly to the humic acid, like the metal ions that have been accumulated from the donor solution (e.g., from the lake water).

Transport Kinetics of DMT. The change of the metal ion concentration in the acceptor solution can be described by (15)

$$[\text{Me}]_{\text{acc},t} = [\text{Me}]_{\text{acc},t=0} + ([\text{Me}]_{\text{acc},t=\infty} - [\text{Me}]_{\text{acc},t=0})(1 - e^{-bt})$$

$$t_{1/2} = \frac{\ln 2}{b} \quad (\text{when } [\text{Me}]_{\text{acc},t=0} = 0) \quad (1)$$

in which $[\text{Me}]_{\text{acc},t}$ is the metal concentration in the acceptor solution at time t , $[\text{Me}]_{\text{acc},t=0}$ is the metal concentration in the acceptor solution at time 0, $[\text{Me}]_{\text{acc},t=\infty}$ is the metal concentration in the acceptor solution at the Donnan membrane equilibrium, and b is a constant related to the ion transport kinetics. $t_{1/2}$ is the time needed for the acceptor to reach half the concentration at equilibrium.

Because of the low free metal concentrations in natural waters, it might be the case that for some metal ions, equilibrium has not been reached yet within 2 or 3 days. In that case, the free metal ion concentration can be calculated according to the following formula (16), which can be applied in the case of membrane diffusion-limited transport

$$[\text{Me}^{z+}]_{\text{don}} = \frac{V_{\text{acc}} \delta_m}{A_e D_m B^z} \frac{[\text{Me}]_{\text{acc},t} - [\text{Me}]_{\text{acc},t=0}}{t} \quad (2)$$

in which $[\text{Me}^{z+}]_{\text{don}}$ is the free metal concentration in the sample (donor) (mol/m³), V_{acc} is the acceptor volume (m³), A_e is the effective surface area of the membrane (m²), δ_m is the thickness of the membrane (m), D_m is the diffusion coefficient of the free metal ion in the membrane (m²/s), B is the Boltzmann factor for the Donnan phase in the membrane (–), z is the charge of the metal ion, $[\text{Me}]_{\text{acc},t}$ (mol/m³) is the total metal concentration in the acceptor at sampling time t , $[\text{Me}]_{\text{acc},t=0}$ is the total metal concentration in the acceptor at $t = 0$ (residual concentrations), and t is the deployment time (s).

To verify whether a certain metal ion reached Donnan membrane equilibrium in the DMT, the results of eq 2 are compared to the results assuming equilibrium. If the free metal ion concentration calculated with eq 2 is higher than the result calculated by assuming equilibrium, Donnan membrane equilibrium has not been reached yet, and a kinetic approach has to be used (eq 2).

Measuring Free Metal Ion Concentrations in Synthetic Waters. The DMT method was tested in the lab using synthetic waters. In the first test series, the donor solution (30 L) consisted of 1 mM Ca(NO₃)₂ and a variable amount of Cu(NO₃)₂, ranging from 0.03 to 50 μM. No ligands or only 0.11 mM NTA was added as a ligand to the donor side to achieve a free Cu²⁺ concentration ranging from 0.125 nM to 1.3 μM, which were measured by both lab and field DMT cells. In the second test series donor solutions were prepared that contain various concentrations of Cu, Cd, Ni, Pb, and Zn in the presence of NTA. At several time steps, samples were taken from both the donor and the acceptor for the field-DMT, usually with a maximum of 4–8 days. The measured free ion concentrations in both experiments 1 and 2 were then compared to the predictions using speciation models.

In all lab experiments, 30 mg/L of purified humic acid and 1 mM $\text{Ca}(\text{NO}_3)_2$ was used in the acceptor side. The humic acid was purified from forest floor material taken from the Tongbersven forest in The Netherlands (18). Nitrilotriacetic acid (NTA) was of analytical grade (Merck) as well as the metals, which were added as nitrate salts. All materials involved in the DMT experiments were acid and water washed before use. Cu, Cd, Zn, Ni, and Pb concentrations were measured on ICP-MS (Perkin-Elmer; Elan 6000); Ca, K, and Na concentrations on ICP-AES (Spectro, Spectroflame); and humic acid concentrations on a DOC/TOC analyzer (Skalar; SK12). Either K or Na was added as nitrate salt for the correction of salt differences between donor and acceptor. pH was measured by a combined glass electrode (PHM210, Radiometer Analytical).

Measuring Free Metal Ion Concentrations in Natural Waters. When the DMT method is used in situ to measure free metal ion concentrations in natural waters, the field cells are attached to a floating life buoy, which is attached by a rope to the shore or to the bottom by means of an anchor. By using this life buoy, measurements at different depths below the water surface are possible. Several cells are used in practice at the same depth, and at each sampling time, two cells are taken out of the water and sampled. All materials used for the sampling had been washed in acid previously. Water samples as well as the DMT cells were taken in metal-free boxes to the laboratory to minimize contamination.

In August and September 2003, several total and free metal ion concentrations have been measured in the River Rhine in The Netherlands (near Wageningen) at 50 cm depth, in the stream Furtbach in Switzerland at 50 cm depth, and in Lake Greifen in Switzerland at 2.5, 5, and 10 m depth. In February 2004, these measurements have been repeated in the River Rhine to have measurements in two different seasons. In April 2004, total and free metal ion concentrations have been measured in the River Wyre in the UK at 30 cm depth. In addition, in June 2004, a 4 day measurement under fluctuating water temperatures was done in the River Rhine.

Like in the experiments with synthetic waters, 30 mg/L of purified humic acid was added to the acceptor side, which contained $\text{Ca}(\text{NO}_3)_2$ at a similar ionic strength as the donor solution. For measurements of total metal concentrations, water samples were taken every day of the exposure period and were filtered at $0.45\ \mu\text{m}$ (Aquatron 30, Schleicher and Schuell). DOC samples were taken from the filtered water samples and analyzed on a DOC/TOC analyzer. Samples were further treated similarly as described in the previous section.

Model Calculations. All calculations were executed using the computer program ECOSAT (19), in which the relevant inorganic ion complexes are accounted for using the reaction constants in the database of this program. Also, for the calculation of complexation of Cu, Cd, Ni, Zn, and Pb with NTA, exchange constants ($\log K$ values) have been used according to the ECOSAT database (see Table S2, Supporting Information).

For natural water systems, it is always problematic how to model metal binding to natural organic matter (6). We have not analyzed the composition of the DOC, so assumptions have to be made about the nature of the dissolved organic matter. For example, one may assume that part of the organic matter consists of humic acid and part of the organic matter consists of fulvic acid. Moreover, it can also be assumed that part of the organic matter is inert for metal binding. After making the assumptions about the organic matter, metal binding to DOC can be modeled. For the calculation of metal complexation with humic and fulvic acid like fractions from the natural water systems, the NICA–Donnan model was used (6) using generic parameters (see Table S3, Supporting Information).

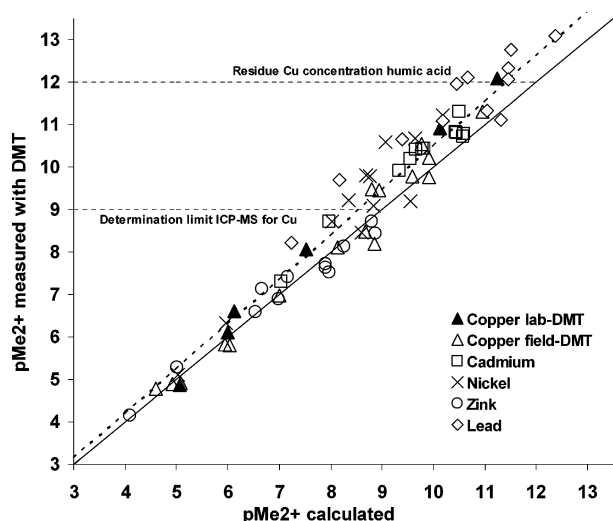


FIGURE 1. Comparison between calculated and measured free ion concentrations. Only Cu results of the lab DMT are shown; all the other free metal ion concentrations were measured by field-DMT. The diagonal solid line is the 1:1 line, whereas the dotted line represents the linear regression of all the data ($p[\text{Me}^{2+}]_{\text{DMT}} = 1.05 p[\text{Me}^{2+}]_{\text{calculated}}$). The horizontal dotted lines represent the detection limit for Cu on ICP-MS and the residue concentration of Cu in the humic acid used in the acceptor side of the DMT.

The purified humic acid that was used as a ligand for the acceptor side has been included in the dataset to derive the generic parameters by Milne et al. (20). However, for H, Cu, Ca, Cd, Ni, and Zn complexation to the purified humic acid used in this study, parameters specific for this particular humic acid have been determined. For complexation of Pb with humic acid, no specific parameters have been derived yet, and therefore, the generic parameters have been used (see Table S3, Supporting Information).

Results and Discussion

Free Metal Ion Concentration in Synthetic Solutions. A range of free Cu^{2+} concentrations has been measured by the field and lab cell DMT. The calculated and measured Cu^{2+} concentrations match well, for the lab cells as well as for the field cells (Figure 1). In the range between $[\text{Cu}^{2+}] = 10^{-9} - 10^{-12}\ \text{M}$, which is lower than the determination limit of the ICP-MS, it is necessary to use a ligand in the acceptor side.

After testing Cu in a monocomponent system, multicomponent systems were tested. Free metal ion concentrations were measured with the field cell and compared to the calculated free metal ion concentrations in solution. In the concentration range from 10^{-4} to $10^{-13}\ \text{M}$, calculations and measurements are in good agreement (Figure 1). At very low metal concentrations, the agreement between measured and modeled values is slightly less good, and the lead concentration is slightly underestimated by the DMT. This might be due to the lack of specific parameters for Pb binding to the humic acid used in the acceptor side. The overall regression line between measured and modeled values has a slope of 1.050 ± 0.007 , which implies that measured and calculated values differ on average from 0.2 log units (factor 1.5) in the higher concentration range ($>10^{-5}\ \text{M}$) up to 0.5 log units (factor 3) in the higher concentration range ($<10^{-10}$) (Figure 1). All results in Figure 1 were measured at the equilibrium situation. For cases in which a kinetic approach has to be used, Weng et al. (16) showed agreement between measured and modeled values.

Free Metal Ion Concentrations in Natural Waters. Some characteristics and dissolved major cation concentrations of the natural waters, in which free metal ion concentrations

TABLE 1. Electric Conductivity (EC), Ionic Strength (I), Dissolved Organic Carbon (DOC), pH, and Dissolved Major Cation Concentration in the River Rhine, the Stream Furtbach, the Lake Greifen, and the River Wyre^a

	EC ($\mu\text{S}/\text{cm}$)	I (mM) ^b	DOC (mg/L)	pH	Ca (mM)	K (mM)	Mg (mM)	Na (mM)
Rhine summer	750 (18)	12.00 (0.29)	4.0 (0.4)	7.86 (0.20)	1.68 (0.04)	0.14 (0.02)	0.49 (0.01)	2.81 (0.41)
Rhine winter	669 (0)	10.70 (0.00)	3.3 (0.6)	7.73 (0.24)	1.81 (0.08)	0.14 (0.02)	0.42 (0.02)	2.03 (0.08)
Furtbach	617 (29)	9.87 (0.47)	2.2 (0.4)	8.11 (0.08)	2.35 (0.06)	0.08 (0.01)	0.85 (0.05)	0.46 (0.01)
Greifen 2.5 m	336 (3)	5.37 (0.05)	4.2 (0.1)	8.66 (0.03)	0.73 (0.04)	0.09 (0.00)	0.60 (0.02)	0.67 (0.02)
Greifen 5 m	335 (4)	5.36 (0.06)	4.2 (0.0)	8.66 (0.02)	0.72 (0.03)	0.11 (0.02)	0.60 (0.01)	0.67 (0.02)
Greifen 10 m	486 (1)	7.77 (0.01)	3.2 (0.1)	7.72 (0.00)	1.59 (0.00)	0.07 (0.00)	0.62 (0.01)	0.57 (0.00)
Wyre	103 (—)	1.64 (—)	7.3 (0.6)	7.59 (1.17)	0.42 (0.05)	0.03 (0.00)	0.10 (0.01)	0.31 (0.02)

^a Standard deviation is given in parentheses. ^b I was calculated by $I = 1.6 \times 10^{-5} \times \text{EC}$ (30).

TABLE 2. Total and Free Metal Concentrations in the River Rhine (at 0.5 m), River Furtbach (at 0.5 m), Lake Greifen (at 2.5, 5, and 10 m), and River Wyre (at 0.3 m)^a

	pCd (M)	pNi (M)	pPb (M)	pCu (M)	pZn (M)
Rhine summer 0.5 m					
total ($n = 5$)	9.29 (0.17)	7.23 (0.05)	8.95 (0.08)	7.12 (0.02)	6.55 (0.05)
free ($n = 5$)	10.80 (0.07)	8.52 (0.20)	12.11 (0.56) ^b	10.94 (0.16) ^b	7.45 (0.17)
free predicted ^c	10.54	7.86	11.61	10.72	6.91
Rhine winter 0.5 m					
total ($n = 6$)	9.55 (0.05)	7.49 (0.06)	9.28 (0.08)	7.34 (0.05)	6.69 (0.11)
free ($n = 4$)	10.65 (0.19)	8.81 (0.13)	12.05 (0.30) ^b	10.93 (0.37) ^b	8.06 (0.55)
free predicted ^c	10.87	8.15	13.35	12.02	7.05
Furtbach 0.5 m					
total ($n = 4$)	9.92 (0.05)	8.20 (0.10)	9.23 (0.34)	7.43 (0.13)	6.91 (0.05)
free ($n = 4$)	11.94 (0.06)	9.60 (0.16)	12.13 (0.06)	10.42 (0.20) ^b	8.18 (0.10)
free predicted ^c	11.31	8.44	13.2	12.71	7.29
Greifen 2.5 m					
total ($n = 2$)	9.81 (0.42)	8.07 (0.08)	9.53 (0.14)	7.63 (0.00)	<d.l. ^d
free ($n = 2$)	11.29 (0.00)	9.84 (0.26)	12.12 (0.19)	10.14 (0.03) ^b	<d.l.
free predicted ^c	12.53	8.88	14.89	15.17	
Greifen 5 m					
total ($n = 2$)	10.23 (0.25)	8.08 (0.02)	9.64 (0.24)	7.62 (0.02)	<d.l.
free ($n = 1$)	11.27 (—)	9.79 (—)	12.36 (—)	10.23 (—) ^b	<d.l.
free predicted ^b	12.71	8.90	15.16	15.15	
Greifen 10 m					
total ($n = 1$)	<d.l.	7.97 (0.00)	9.88 (0.15)	7.87 (—)	<d.l.
free ($n = 2$)	11.05 (0.05)	9.64 (0.15)	11.84 (0.05)	10.07 (0.04) ^b	7.25 (0.02)
free predicted ^c		8.20	14.22	12.63	
Wyre 0.3 m					
total ($n = 4$)	9.06 (0.30)	7.75 (0.04)	8.96 (0.09)	7.69 (0.03)	7.55 (0.18)
free ($n = 6$)	<d.l.	9.23 (0.10)	10.67 (0.05)	10.54 (0.06) ^b	8.32 (0.31)
free predicted ^c	10.52	8.25	12.72	13.42	8.50

^a Numbers between parentheses show the standard deviation. All numbers are expressed as pMe ($= -\log[\text{Me}]$). ^b Free metal concentration was calculated by means of the kinetic approach according to eq 2 (ref 16; $V_{\text{acc}} = 12 \times 10^{-6} \text{ m}^3$; $A_e = 3.9 \times 10^{-4} \text{ m}^2$; and $\delta_m = 16 \times 10^{-3} \text{ m}$). ^c Prediction was done by the NICA–Donnan model under the assumption that 80% of the total DOC is fulvic acid and 20% is humic acid (as has been done before in Meylan et al. (25)). ^d <d.l. = the concentration is below the determination limit of ICP-MS.

have been measured, are shown in Table 1. All of the waters have a relatively high pH. The waters range from soft to hard waters, illustrated by the variety in ionic strength. At 10 meters depth, Lake Greifen is anoxic (data not shown). All the other measurements were done in oxic water.

Previous experiments showed that a reaction time of 2 or 3 days is suitable for field measurements using DMT, in which time interval most metal ions have reached the (pseudo) Donnan membrane equilibrium (data not shown). In those cases where the calculated free metal ion concentrations according to the kinetic approach (eq 2) were higher than the measured equilibrium concentration, we used the calculated free metal ion concentration in the sample.

Total dissolved metal concentrations ($<0.45 \mu\text{M}$) vary between the different water systems and ranged between 0.06 and 0.72 nM Cd; 8.4–48 nM Ni; 0.14–1.1 nM Pb; 20–67 nM Cu; and 30–237 nM Zn. During one exposure period, total metal concentrations were fairly constant. The fraction of the total metal concentration that was measured as free

metal ions ranges between 0.95 and 9.1% for Cd^{2+} ; 1.7–5.1% for Ni^{2+} ; 0.069–1.9% for Pb^{2+} ; 0.015–0.63% for Cu^{2+} ; and 4.3–13% for Zn^{2+} (Table 2).

In general, Lake Greifen contained lower total metal concentrations than the three rivers that were studied. Those rivers have similar total metal concentrations. Most of the free metal ion concentrations were similar in the lake and the rivers. Only $[\text{Ni}^{2+}]$ was approximately 0.5 log units (factor 3) lower in the lake than in the rivers.

The total metal concentrations in the River Rhine are higher in summer than in winter. This probably has to do with dilution of the Rhine water in winter due to higher water fluxes in winter than in summer. Nevertheless, the free metal concentrations of Cd^{2+} , Pb^{2+} , and Cu^{2+} were not higher in summer than in winter but were rather constant.

In Lake Greifen, vertical spatial variation of metal concentrations has been analyzed: while the total Cd concentration decreases with depth, the free Cd^{2+} concentration is constant. This implies that Cd availability will probably not

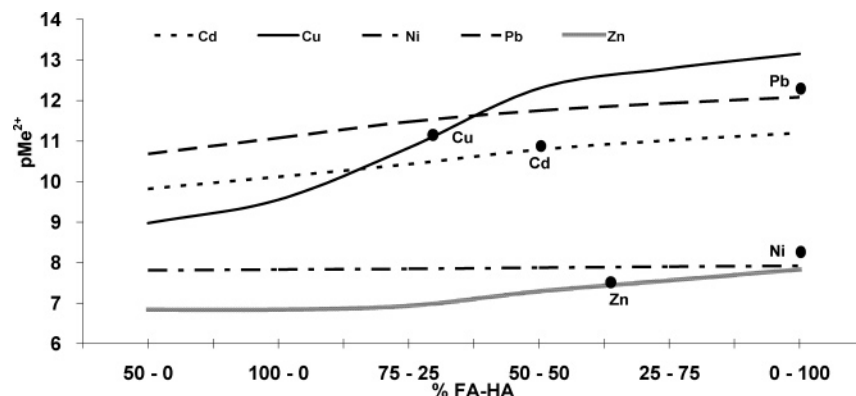


FIGURE 2. Variation in the predicted free metal ion concentrations in the summer in the Rhine when different assumptions about the composition of DOC are used. The assumptions go from 50 and 100% fulvic acid until 100% humic acid. The measured free metal ion concentrations have been added as dots.

vary with depth. The same trend applies to Pb, although the differences are smaller. For the other metal ions, both total and free ion concentrations hardly vary between different water depths.

The free Cd^{2+} concentrations found in Lake Greifen are approximately 1 order of magnitude lower than found by Xue and Sigg (21, 22). They used differential pulse cathodic stripping voltammetry (DPCSV) and measured a pCd^{2+} of 10.1 at similar total Cd levels as in our study. Even though the DOC levels and the pH were somewhat higher in our study, the free Cu^{2+} levels measured by DMT are several orders of magnitude higher than the ones found in Xue and Sigg (22) and Xue and Sunda (23), who found pCu^{2+} concentrations of 14.8 (measured by CLE-DPCSV) in Lake Greifen, at similar total copper concentrations as in our study. The free Cu^{2+} concentrations measured by DMT in the Furtbach Stream are much higher than the ones found by Meylan et al. (24, 25), who used CLE-DPCSV/DPASV and measured pCu^{2+} in the range of 11.5–14, at similar total Cu concentrations as in our study. It has recently been suggested that these voltammetric techniques may underestimate the free copper ion activities because of incomplete equilibration with the competing ligand (26). A more extensive comparison between DMT and other speciation techniques is given by Sigg et al. (27).

Speciation Modeling: Discrepancies and Uncertainties.

In literature, different assumptions are made upon the composition of natural organic matter. For example, to model the free metal ion concentration, Meylan et al. (25) used 20% humic acid and 80% fulvic acid for the Furtbach Stream. Using this assumption leads to predictions that are often different from the measured free metal ion concentration (Table 2). For Ni and Zn, it usually overestimates the free metal concentration, whereas for Pb and Cu, it usually leads to an underestimation. The difference between modeled and measured concentrations also varies among the water systems that were studied.

As an example, Figure 2 shows the variation in the predicted free metal ion concentrations in the summer of 2003 in the Rhine when different assumptions about the composition of the DOC are used. The assumptions go from 100% fulvic acid to 100% humic acid. Besides considering all DOC to be reactive in the metal binding process, one may also consider part of the organic matter to be inert for metal binding. Beyer et al. (28) analyzed the composition of several sources of organic matter and found that only 10–15% of the natural organic matter was fulvic acid and 10–30% was humic acid. Lofts and Tipping (29) used an assumption of 50% fulvic acid and 50% inert, which has been introduced into Figure 2 as well. Especially the predicted free Cu^{2+} concentration varies highly within the different assumptions. A different

assumption about the DOC composition may lead to a predicted free Cu^{2+} concentration of several orders of magnitude of difference. Cd^{2+} , Pb^{2+} , and Zn^{2+} may vary 1 order of magnitude among the different assumptions, whereas Ni^{2+} hardly depends on the assumptions on organic matter. The degree of variation in the predicted free metal ion concentration mainly depends on the binding strength of the metal ion with humic and fulvic acid. Cu binds strongly to humics and fulvics, whereas Ni binds weakly.

The free metal ion concentrations as measured by DMT have been added to Figure 2. To optimize the model calculations to fit the DMT measurements, each metal ion requires a different assumption about the DOC composition. Cu, Pb, Cd, and Zn all have agreement between the model calculations and the measurements at a certain assumption. However, measured free Ni^{2+} is lower than modeled Ni^{2+} no matter what assumptions are done. Apparently, the model did not take a certain Ni-binding agent into account. For the free metal concentration of the Rhine in the summer period, the best overall agreement is obtained when it is assumed that 30% of the total DOC is fulvic acid and 70% is humic acid. The assumption of DOC being 30% fulvic acid, 30% humic acid, and the rest inert (used for DOC in soil solution; ref 7) would generally overestimate the free metal concentration. For the winter period, the best overall prediction is made when 50% of the DOC is assumed to be humic acid and the rest inert.

Because the generic NICA–Donnan parameters for humic and fulvic acids (20) are based upon collected data sets of different authors, there is some uncertainty in model parameters such as $\log \bar{K}$, which is the median exchange constant for metal binding and n , which is the width of the distribution of the median exchange constants. Within a variation of $\log \bar{K}$ of ± 0.1 , the free copper concentration changes less than 0.1 log units (factor 1.25). Because the Cu binding to the phenolic site is stronger than the Cu binding to the carboxylic site, varying the $\log \bar{K}$ value of the carboxylic site hardly influences the free Cu^{2+} concentration. The humic acid from Tongbersven that was used in the acceptor side of the DMT has lower $\log \bar{K}$ values for Cu than the generic humic acid (see Table S3, Supporting Information), leading to higher Cu^{2+} predictions than predictions using generic parameters. It might be that the variation in $\log \bar{K}$ values adds to the uncertainty that modeling free metal ion concentrations caused. However, it is probably not the main cause of the discrepancies between measured and modeled values.

These results indicate that the nature of organic material may differ considerably between different water systems and that it is very difficult to model the binding of metal ions to natural organic matter, among others because model cal-

culations depend strongly on assumptions made on the composition of the organic matter. Therefore, it is important to obtain better insight in the DOC fractions, like the humic and fulvic acid fractions and the fraction of small organic acids. Because of the lack of sufficient binding data for Fe with humic acids, these competition effects can at present not be accounted for with great accuracy. Similarly, the metal ion binding to other colloidal particles present in the aqueous phase, like Fe-(hydr)oxides, can in our opinion also not be accounted for with great accuracy with our present knowledge, and we have therefore also ignored this effect in the speciation modeling. Metal binding to these particles may thus partly also explain the differences between measured and modeled values. Besides the uncertainty in the model calculations, we also have to deal with the uncertainty in the DMT measurements.

Daily Fluctuations in Metal Concentrations. Because of influences such as rain and temperature fluctuations, total and free metal concentration may fluctuate in natural waters, even within a few days. In June 2004, a 4 day measurement of free metal ion concentrations was done in the River Rhine during a temperature (T) drop of 0.8 °C per day, which led to a pH decrease of 0.25 per day ($\text{pH} = 2.38 + 0.28T$; $R^2 = 0.99$).

Free metal ion concentrations changed during those days as a consequence of a decrease in pH and of changes in total metal concentration. Even though the equilibrium time for DMT measurements in natural water is 2–3 days, it appeared to be possible to use DMT for measurements of free metal ion concentrations that change from day to day (see Table S4, Supporting Information). The reason for this is that after the first measurement, all DMT cells are already close to the equilibrium of the following days (fluctuations in free metal ion concentrations are rather small as compared to their absolute value). Therefore, it takes only less than a day to adjust to the new situation.

If the free metal ion concentration in the river changes, we can derive that the time the DMT needs to reach $x\%$ of the new equilibrium situation depends on the b -value of eq 1

$$t_{x\%} = \frac{1}{b} \left[\ln \frac{1}{1-x\%} + \ln \left(1 - \frac{[\text{Me}^{z+}]_{\text{old}}}{[\text{Me}^{z+}]_{\text{new}}} \right) \right] \quad (3)$$

The b -value in natural waters is approximately 0.1 (data not shown). Therefore, an estimation of the time to reach 95% of the new situation would be

$$t_{95\%} = 30 + 10 \ln \left(1 - \frac{[\text{Me}^{z+}]_{\text{old}}}{[\text{Me}^{z+}]_{\text{new}}} \right) \quad (4)$$

As long as the new situation is close to the old situation ($[\text{Me}^{z+}]_{\text{new}}/[\text{Me}^{z+}]_{\text{old}} < 1.1$), it only takes a few hours for the DMT to adjust to the new equilibrium concentration. On the other hand, if the free metal ion concentration doubles instantaneously, it takes approximately 23 h before the new equilibrium has been reached.

So, day/night fluctuations in free metal ion concentrations can only be detected by the DMT if these fluctuations are rather small. If sudden changes are large, DMT needs approximately a day to adjust to the new situation.

This study shows that for several systems, the predictions by NICA–Donnan may differ by several orders of magnitude from the free metal concentrations measured by DMT, mainly because it is still unclear what assumptions should be made for the composition of the dissolved organic matter.

More research is needed where speciation models are combined with in situ measurement of the free metal ion concentration and a more complete analysis of the various

DOC fractions present in the field. The role of inorganic colloids and the role of the binding of monomeric iron to humic substances on metal speciation also deserve more attention.

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Supporting Information Available

Schematic overview of the DMT cell (Figure S1), residual metal concentrations of humic acid from the Tongbersven (Table S1), complexation constants for metal binding to NTA (Table S2), specific and generic NICA–Donnan parameters for humic and fulvic acid (Table S3), and the variation of the free and total metal concentrations under changing temperature and pH conditions (Table S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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