



Size Fractionation (Dissolved, Colloidal and Particulate) of Trace Metals in the Thur River, Switzerland

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Abstract. The distribution of some trace metals (Cu, Zn, Ni, Co, Fe, Mn) and of DOC over a particulate ($> 1 \mu\text{m}$), a colloidal (size $< 0.45 \mu\text{m}$ and molecular weight $> 10 \text{ kD}$) and an ultrafiltered fraction ($< 10 \text{ kD}$) was determined at several sites on the Thur River, Switzerland, at various times of the year. The complexation of Cu by strong ligands in the ultrafiltrate and in the conventional filtrate ($< 0.45 \mu\text{m}$) was compared using a ligand-exchange/CSV method.

The $< 0.45 \mu\text{m}$ concentrations of Cu (from an average of 7 nM to 24 nM), Zn ($< 5\text{--}23 \text{ nM}$), Ni (5–13 nM), Co (1.5–3 nM) and Mn (7–92 nM) increased downstream. The major part of Cu, Zn, Ni and Co usually occurred in the ultrafiltrate fraction at all sites, whereas Fe and Mn were mostly in the particulate fraction, under conditions of low suspended matter content ($< 10 \text{ mg L}^{-1}$) in the river. The percentage of metal in the colloidal fraction, with respect to the $0.45\text{-}\mu\text{m}$ filtrate, decreased in the order: Cu (median 11%) $>$ Zn \approx Ni (median 5–6%) $>$ Mn \approx Co (median $< 5\%$). DOC also consisted mostly of molecules in the $< 10 \text{ kD}$ range.

Cu was strongly complexed by natural organic ligands in all filtrate and ultrafiltrate samples. A large part of the strong Cu binding ligands consisted of compounds in the $< 10 \text{ kD}$ range, but colloidal ligands with similar properties also occurred. Cu was distributed among the dissolved and the colloidal ligands, roughly in proportion to organic carbon. The colloidal fraction (as defined here) did not increase in its proportional amount downstream and was only of limited significance in transporting trace elements in the Thur River under low discharge conditions.

Key words: river water, trace metals, colloids, Cu complexation

1. Introduction

The size distribution of trace metals and their complexation by organic ligands are two complementary aspects of their speciation, which are significant with regard to their fate and their impact on organisms. Size fractions may in natural waters range from small molecules to particles in the millimeter range. Metals bound to large particles will quickly be transported to the sediments, and may later be released by resuspension of the sediments or by chemical changes. Metals bound to ligands in dissolved form have a long residence time in water and may be transported over

long distances in rivers. Metals bound in the colloidal size range (from few nanometers to about one micrometer) should exhibit an intermediate behavior, since very small particles settle very slowly, but may eventually aggregate into larger ones.

The role of the colloidal size range in binding metals or nutrients has recently been studied in various aquatic systems (Benoit et al., 1994; Buffle et al., 1992; Hilger et al., 1999; Kraepiel et al., 1997; Martin et al., 1995; Perret et al., 1994; Ross and Sherrell, 1999; Rostad et al., 1997; Sañudo-Wilhelmy et al., 1996; Stordal et al., 1996; Wells et al., 1998; Wen et al., 1996, 1997, 1999; Wilkinson et al., 1997). The major part of these studies concerns marine and estuarine systems, whereas little is known about freshwater rivers, especially those impacted by inputs from sewage and from agricultural runoff.

Studies of the complexation of trace metals by organic ligands, using e.g., electrochemical methods combined with ligand exchange, yield information on the complex stabilities and natural ligand concentrations (Van den Berg, 1984; Xue and Sigg, 1993). The combination of the two approaches of size distribution and investigation of the complexation of trace elements provides information about the nature of the ligands, especially their molecular weight range (Wells et al., 1998).

Reliable data on trace metal concentrations in rivers are still rather limited to few geographical areas and to rivers with little or no significant anthropogenic inputs (Benoit, 1994, 1995; Coale and Flegal, 1989; Hurley et al., 1995, 1996; Shafer et al., 1997, 1999; Shiller, 1997; Shiller and Boyle, 1985; Windom et al., 1991).

In the present work we investigate how the concentrations, size distribution and speciation of some trace metals (Cu, Zn, Ni, Co, Fe, Mn) in the Thur River, eastern Switzerland vary with increasing inputs from sewage and agriculture. The Thur River runs from alpine background through a densely populated region and intensively used agricultural land. The metal concentrations and size distributions are compared at four sites representative of different pollution levels. The size distribution of metals is examined over a particulate (particle diameter $>1 \mu\text{m}$), a colloidal (particle diameter $<0.45 \mu\text{m}$ and molecular weight $>10 \text{ kD}$) and a dissolved fraction (molecular weight $<10 \text{ kD}$). This approach is combined with the investigation of the complexation of copper using a ligand-exchange/voltammetric method, which provides insight into the size distribution of copper complexing ligands. The origin and nature of the colloidal fraction and of the dissolved ligands in this system are discussed.

2. Experimental Part

2.1. SAMPLING SITES

All sampling sites are situated within the catchment of the Thur River, eastern Switzerland. The Thur River runs from the alpine region Toggenburg to the Rhine River, over a total length of 134 km, a catchment area of total 1696 km^2 , with about 340 000 inhabitants (Jakob et al., 1994).

Four sampling sites were selected along the Thur River to represent the different parts of the catchment with various pollution levels and the influence of agricultural and industrial inputs. The uppermost station Necker is situated on a tributary of the Thur River and represents a background site with mostly alpine meadows in the catchment area; the population density in this part of the catchment is less than 10 inhabitants per km². The site Lütisburg represents the upper part of the catchment of the Thur River, with alpine meadows and touristic activities. The site Schönenberg is located on the Thur River, downstream of inputs from an industrialized region. The site Andelfingen lies downstream close to the confluence with the Rhine River and is affected by inputs from agriculture and sewage; the average population density in the whole catchment is about 200 inhabitants per km². The long-term average discharge rates are: Necker at the nearest water level measurement station (about 7 km downstream of the sampling site) 3.2 m³/s; Lütisburg 20.8 m³/s; Schönenberg 38.5 m³/s; Andelfingen 46.8 m³/s (Landeshydrologie, 1997). The geochemical background of the catchment area mostly consists of sedimentary carbonate rocks and does not markedly differ among the various sites. Conglomerated rocks of more variable composition are present in some parts of the upper catchment, including the Necker catchment. Sampling dates were distributed over the year. The hydrological conditions were in most cases close to base-flow conditions, with discharges lower than the above average values, with exception of the sampling on 5/5/1998, on which discharges were close to the average value.

2.2. SAMPLING AND SIZE FRACTIONATION

Separation of river water into three operationally defined size classes, a particulate, a colloidal and a dissolved fraction was performed using continuous-flow centrifugation, membrane filtration and cross-flow ultrafiltration. The particulate fraction consists of particles with a diameter larger than about 0.45–1 μm collected by continuous centrifugation. Colloids are defined as submicron particles or macromolecules which have a diameter < 0.45 μm and a molecular weight > 10 kD. The dissolved fraction (ultrafiltrate) is defined as the size range of molecules and ions which pass a 10 kD membrane. The distinction between the colloidal and the dissolved fraction is operationally defined according to the cross-flow ultrafiltration device used and to the theoretical cut-off of 10 kD.

Sampling was performed at least at 1 m distance from the bank at a water level approximately 20 cm below the surface. The river water was sampled continuously with a peristaltic pump with teflon and partly silicone tubing (at about 1.5 L min⁻¹) and directly centrifuged. The centrifuge (LE 402-18091, CEPA) was operated at 25000 rpm with a flow rate of 1.2 L min⁻¹. Previous investigation of this system has shown that the cut-off range of the centrifuge was about 1 μm as a function of the morphology and density of the particles (Hilger, 1998). Particles > 1 μm were collected on a teflon sheet covering the cylinder inside the centrifuge. The inlet port was made of teflon, all tubes consisted of either silicone or teflon, the retentate

vessel and connecting pieces consisted of polypropylene (PPE). The teflon sheets were transported to the laboratory in the original container. The particles were collected from the teflon sheets as concentrated suspensions using nanopure water under clean-bench conditions and were subsequently freeze-dried, including the water used for collection. The teflon sheets and the whole centrifuge set-up with the tubings were carefully cleaned in the lab with diluted HNO_3 and nanopure water before each sampling campaign.

To avoid contamination from the centrifuge, separate samples for ultrafiltration were collected directly into a filtration unit with a $0.45\text{-}\mu\text{m}$ filter. The difference between the cut-off particle size of the centrifuge and that of the $0.45\text{-}\mu\text{m}$ filtration is considered as negligible, but this procedure may be responsible for some losses of material in this size range. The $< 0.45\text{-}\mu\text{m}$ filtrate (about 1 L) was used for fractionation into an ultrafiltrate and a colloidal retentate fraction, using a cross-flow ultrafiltration device (Millipore Minitan) equipped with a 10-kD polysulfone membrane. Concentration factors for the colloidal retentate (size fraction $< 0.45\ \mu\text{m}$ and $> 10\ \text{kD}$) ranged between 5 and 10, for a duration of about one hour. All these separation steps were carried out immediately in the field with minimal contact to the ambient air. The ultrafiltration system was rinsed with NaOH and nanopure water after each sampling.

The samples were collected in polypropylene bottles, which had been cleaned and prepared under clean-bench conditions and which contained an aliquot of suprapure HNO_3 to result in about $0.01\ \text{M}\ \text{HNO}_3$ (final pH 2.2–2.3) in the final volume for total metal analysis. The bottles were protected with plastic bags in the field. Aliquots of the filtrates, ultrafiltrates and colloid retentates, as well as of total unfiltered samples were thus acidified in the field and subsequently used for total metal analysis. The samples for Cu speciation ($0.45\ \mu\text{m}$ filtrates and ultrafiltrates) were kept at their original pH in polypropylene bottles. Additional samples were collected in glass bottles for DOC and for suspended solids measurement.

Field blanks (bottles treated in the same way as samples) were taken on a regular basis. Blank values of the filtration and ultrafiltration systems were $< 0.03\ \mu\text{g}\ \text{L}^{-1}$ Cu, $< 0.01\ \mu\text{g}\ \text{L}^{-1}$ Ni, Co and Mn, whereas in some cases higher Zn (up to $0.3\ \mu\text{g}\ \text{L}^{-1}$) and Fe (up to $0.5\ \mu\text{g}\ \text{L}^{-1}$) concentrations were observed in the ultrafiltered blanks.

2.3. ANALYTICAL METHODS

Cu, Zn, Ni, Co, and Mn were measured by ICP-MS (Perkin-Elmer Elan 5000) in acidified total, filtrate, ultrafiltrate and colloidal retentate samples without further pretreatment. Rh was added as an internal standard to all samples. Fe was measured by graphite furnace AAS (Perkin-Elmer 5100/ZL). The detection limits were $0.01\ \mu\text{g}\ \text{L}^{-1}$ Cu, Ni, Co, Zn and Mn and $0.1\ \mu\text{g}\ \text{L}^{-1}$ Fe. Ca and Mg were measured by ICP-OES (Spectro). The accuracy of the metal determinations by ICP-MS is checked on a regular basis using the SLRS-3 standard (National Research Council

Canada). The precision of the measurements in each of the fractions is estimated to $\pm 0.05 \mu\text{g L}^{-1}$ for Cu, Ni and Mn, $\pm 0.02 \mu\text{g L}^{-1}$ for Co, $\pm 0.1 \mu\text{g L}^{-1}$ for Zn and $\pm 0.2 \mu\text{g L}^{-1}$ for Fe.

Particles were freeze-dried. Aliquots of the dry particles (50 mg) were digested in a microwave oven (Microwave Laboratory Systems, mls 1200 mega) with concentrated nitric acid (suprapure, 5 mL) and hydrogen peroxide (2 mL) for 20 minutes at temperatures up to 200 °C. The accuracy of the digestion procedure is regularly checked with a reference sediment. The digested solutions were analyzed by ICP-MS.

Organic carbon in the 0.45- μm filtrate, the ultrafiltrate and the colloid retentate was measured with a high-temperature carbon analyzer (Shimadzu Total Organic Carbon Analyzer TOC 500, ASI 502). The precision is estimated to $\pm 0.2 \text{ mg L}^{-1}$. The suspended solid (SS) content was determined gravimetrically using 1 L volume; precision is about $\pm 0.5 \text{ mg L}^{-1}$. Particulate organic C and N were measured with a CHN-analyzer in few samples with sufficient amount of particulate material.

2.4. CU COMPLEXATION

The complexation of Cu in filtered ($< 0.45 \mu\text{m}$) and ultrafiltered ($< 10 \text{ kD}$) samples was determined by ligand-exchange with catechol and cathodic stripping voltammetry as described in detail in Xue and Sunda (1997) and Xue and Sigg (1993). The method is based on ligand-exchange equilibrium between added catechol and natural ligands in samples. The concentration of Cu-catechol complexes is measured by adsorptive differential pulse cathodic stripping voltammetry (DPCSV). Water samples are titrated with Cu, and the concentration of Cu-catechol complexes is measured at each point. Concentrations of free cupric ion [Cu^{2+}] and of natural Cu species [Cu_7^*] are determined at each titration point from equilibrium calculations and mass balance. A data set of [Cu^{2+}] and corresponding [Cu_7^*] is then fitted using the chemical equilibrium fitting program FITEQL (Westall, 1982). A one-ligand model was found to fit most of Thur River samples within the relatively narrow Cu titration range. The conditional stability constant and the ligand concentration are obtained as a set of fitting parameters, and the ambient free cupric ion concentration is calculated using these parameters.

To obtain DPCSV titration data for Cu complexation in a sample, a series of subsamples were spiked with different Cu concentrations (10-250 nM). Aliquots of 25 mL were pipetted into a series of 50 mL high-density polyethylene beakers and buffered with 6 mM HEPES buffer. All the working pH's for the river samples were close to the ambient values (about 8–8.5). The series was allowed to equilibrate at $22 \pm 2^\circ\text{C}$ overnight.

DPCSV analysis was performed with a hanging mercury drop electrode, an Ag/AgCl reference, and a graphite counter electrode. The electrodes were held in a 647 VA stand linked to a 646 VA processor, all made by Metrohm. When the

subsamples were exposed to the electrodes, they were purged with suprapure N₂ gas for 5 min to remove O₂, amended with addition of catechol and equilibrated for another 5 min under N₂ atmosphere with stirring. Adsorptive collection onto the hanging mercury electrode was conducted at a potential of -50 mV for 2 min with stirring, and at rest for 15 s. A cathodic scan was then performed to generate a curve for reduction current versus potential, with the following parameters: initial potential of -50 mV; pulse height of 50 mV; scan rate of 10 mV s⁻¹.

2.5. CALCULATION OF THE SIZE FRACTIONS AND MASS BALANCES

The concentrations in the particulate, colloidal and dissolved fractions and the mass balances were calculated as follows:

$$Me_{\text{tot}} = Me_{\text{part}} + Me_{\text{coll}} + Me_{\text{UF}} \quad (1)$$

$$Me_{\text{filt}} = Me_{\text{coll}} + Me_{\text{UF}} \quad (2)$$

$$Me_{\text{part}} = SS \times PMe, \quad (3)$$

where Me_{tot} = total metal concentration (nM), Me_{filt} = filtered metal concentration (nM), Me_{part} = particulate metal concentration (nM), Me_{coll} = colloidal metal concentration (nM), Me_{UF} = ultrafiltered metal concentration (nM), SS = suspended solid content (g L⁻¹), PMe = Me content in particles (> 1 μm) (nmol g⁻¹).

Me_{coll} was calculated as:

$$Me_{\text{coll}} = (Me_{\text{ret}} - Me_{\text{UF}})/cf \quad (4)$$

where Me_{ret} = Me concentration in colloid retentate (nM), cf = concentration factor, calculated from the total water volume used for ultrafiltration divided by the final retentate volume.

The sums of the colloidal and ultrafiltered fractions (Me_{filt}) were compared to the concentrations measured directly in the 0.45-μm filtrates.

3. Results

3.1. MASS BALANCES OF THE ULTRAFILTRATE, COLLOIDAL AND PARTICULATE FRACTIONS

The mass balances of the sum of the colloidal and ultrafiltrate (< 10 kD) fractions in comparison to the 0.45-μm filtrate (average of 5–7 samples), calculated according to equations (2) and (4), are shown in Table 1 for Fe, Mn, Cu, Ni, Co, Zn and DOC. Reasonable mass balances are obtained for DOC, Co, Ni, Cu and Mn, with occasional larger errors. The size fractionation results of Zn and Fe are affected by contamination, mostly at the uppermost station Necker with the lowest concentrations (≤5 nM Zn and ≤30 nM Fe in the 0.45 μm-filtrate), and to a lesser extent

Table I. Ratios of the sum of ultrafiltered and colloidal fractions to 0.45- μm -filtered samples: (average of 5-7 samplings)

Sites	Necker	Lütisburg	Schönenberg	Andelfingen
Fe		1.2 ± 0.7	0.8 ± 0.4	1.2 ± 0.4
Mn	1.4 ± 0.6	1.2 ± 0.4	1.06 ± 0.19	1.02 ± 0.19
Cu	1.15 ± 0.35	1.01 ± 0.29	1.05 ± 0.23	1.03 ± 0.13
Ni	1.3 ± 0.5	1.07 ± 0.39	1.08 ± 0.31	0.99 ± 0.22
Co	1.13 ± 0.44	1.06 ± 0.58	0.97 ± 0.09	0.98 ± 0.03
Zn		0.97 ± 0.12	1.1 ± 0.5	1.16 ± 0.41
DOC	1.00 ± 0.28	0.94 ± 0.22	0.92 ± 0.09	0.96 ± 0.12

also at the other stations. Poor mass balances in some of the samples for the other elements appear to be related to contamination in one of the fractions (ultrafiltrate, colloidal fraction or $<0.45 \mu\text{m}$ -filtrate). The colloidal fraction is preconcentrated and therefore the measured concentrations are actually higher than those finally calculated; colloidal fractions larger than about 10% of the $0.45 \mu\text{m}$ -filtrate can reasonably be measured. The error in the colloidal fraction in individual samples is estimated to $\pm 20\%$. The major part of the results concerning DOC, Cu, Ni, Co and Mn are within the mass balance range of $100 \pm 20\%$. In the following, only results within this error range are presented and discussed.

Mass balances of the total samples versus the sum of all fractions could not be accurately checked because of incomplete release of elements from the particles in the total acidified samples. The influence of incomplete sampling of the size range $0.45 \mu\text{m}$ to $1 \mu\text{m}$ could not be quantitatively evaluated, but is probably negligible.

3.2. DISTRIBUTION OF ELEMENTS IN THE ULTRAFILTRATE, COLLOIDAL AND PARTICULATE FRACTIONS

The distributions of DOC, Fe, Mn, Cu, Zn, Ni and Co over the ultrafiltered, colloidal and particulate fractions at the four sampling sites are presented in Figures 1–3. The concentrations in the particulate, colloidal and ultrafiltered fractions are measured respectively calculated as indicated above in the Equations (1)–(4). Only samples with a mass balance in the range of $100 \pm 20\%$ for the sum of colloidal and ultrafiltered fractions in comparison to the $0.45 \mu\text{m}$ -filtrate are shown in these figures. Only the filtered ($<0.45 \mu\text{m}$) and the particulate fractions of Fe are shown, because of uncertainties in the ultrafiltration procedure for Fe.

DOC is mostly found in the ultrafiltered fraction at all stations, with about 5 to 20% in the colloidal fraction. DOC generally increases downstream, from an average of 1.3 mg L^{-1} in the Necker to 2.6 mg L^{-1} in Andelfingen (Figure 1). Fe is mostly bound in particles; despite uncertainties in the mass balances, it was

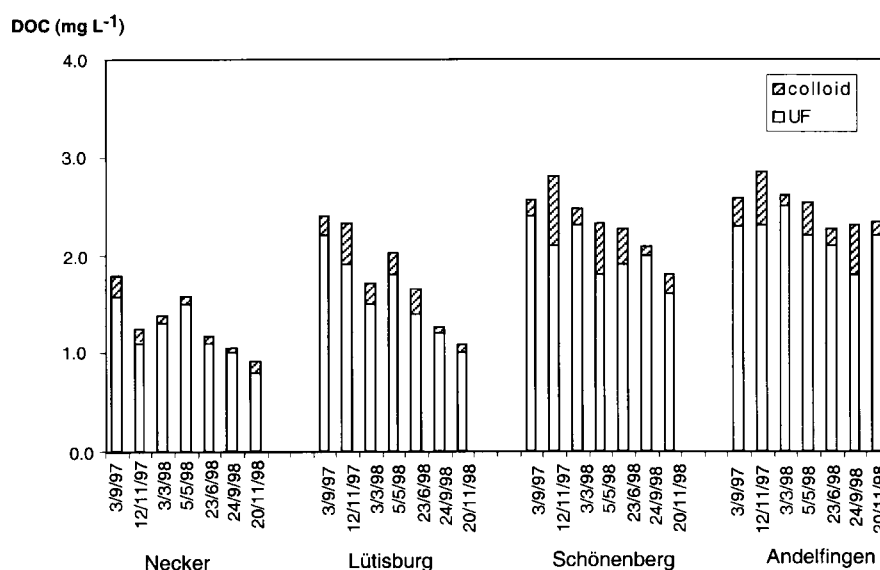


Figure 1. Organic carbon in the ultrafiltrate fraction (UF; < 10 kD) and in the colloidal fraction (coll; > 10 kD and < 0.45 μm) at the four sampling sites on the Thur River on 7 sampling dates.

clear that colloidal Fe represents a substantial part of the < 0.45 μm fraction. Fe in the < 0.45 μm fraction increases downstream, from an average of 30 nM at the Necker site to 85 nM in Andelfingen. Variations of the particulate fraction are mostly related to the suspended solids concentrations, since the Fe content in the particles varies only within a small range (see below) (Figure 2). The particulate fraction also represents a substantial part of Mn, whereas the colloidal fraction is in most cases < 10% of the < 0.45 μm Mn (Figure 2). Mn in the < 0.45 μm fraction increases from an average of 7 nM at the Necker to 92 nM in Schönenberg and 24 nM in Andelfingen.

Dissolved and total Cu clearly increase downstream from an average of 7 nM dissolved Cu at the background site to 24 nM in Andelfingen. Most Cu is usually in the < 10 kD size range; the colloidal fraction represents 5 to about 30% of Cu in the < 0.45 μm fraction and the particulate fraction amounts to only few percents (average about 10%) of the total Cu (Figure 3). Ni and Zn exhibit similar patterns as Cu, but with larger fractions in the particulate size range. These two elements also clearly increase downstream, Ni from an average of 5 nM at the Necker to 13 nM in Andelfingen and Zn from < 5 nM to 23 nM (< 0.45 μm). Both Ni and Zn are mostly in the ultrafiltrate size range, whereas the colloidal Zn fraction ranges from < 1 to about 40% (median 5%) of the < 0.45- μm -filtrate and the colloidal Ni fraction from < 1% to 12% (median 6%) (Figure 3). The dissolved and total Co concentrations also slightly increase downstream, with 1-2 nM dissolved Co at the Necker and about 3 nM in Andelfingen. Most Co is in the < 10 kD range, with

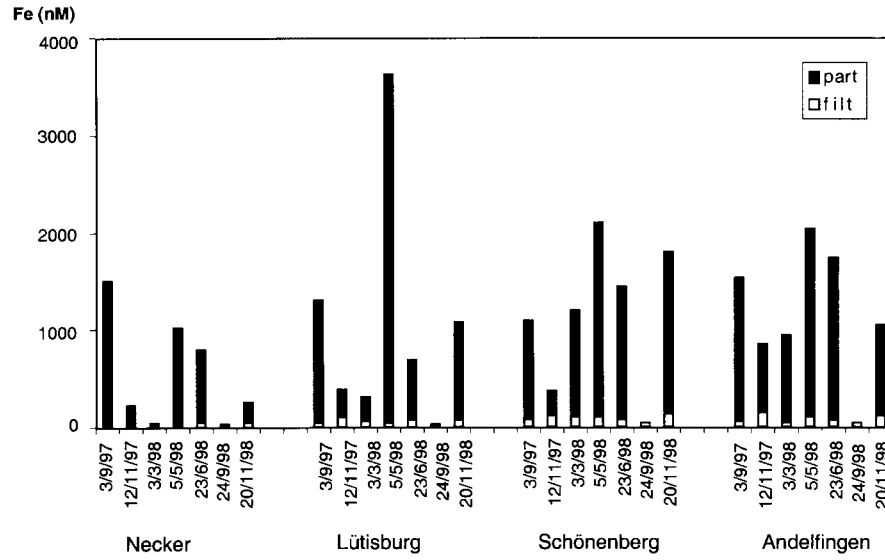


Figure 2a. Fe (a) in the filtered ($<0.45 \mu\text{m}$) and the particulate fraction ($> 1 \mu\text{m}$) and Mn (b) in the ultrafiltrate fraction (UF; $< 10\text{kD}$), the colloidal fraction (coll; $> 10 \text{kD}$ and $< 0.45 \mu\text{m}$) and the particulate fraction ($> 1 \mu\text{m}$) at the four sampling sites on the Thur River on 7 sampling dates. Samples with poor Mn mass balance are left out.

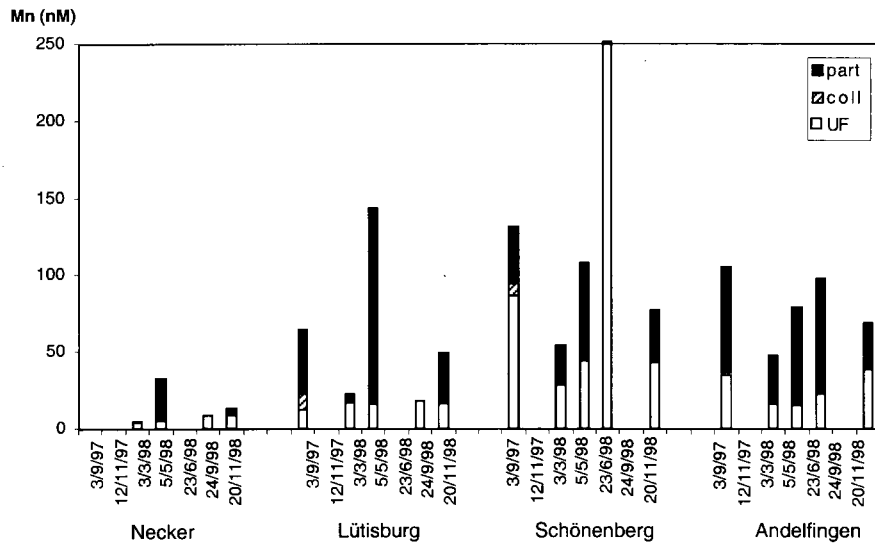


Figure 2b.

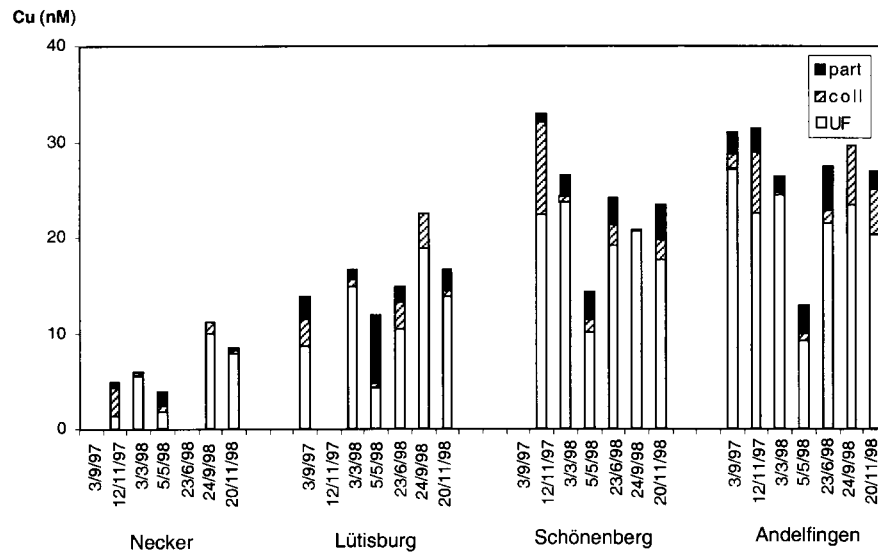


Figure 3a. Cu (a), Zn(b), Ni (c) and Co (d) in the ultrafiltrate fraction (UF; <10 kD), the colloidal fraction (coll; >10 kD and <0.45 μm) and the particulate fraction (>1 μm) at the four sampling sites on the Thur River on 7 sampling dates. Samples with poor mass balances are not shown.

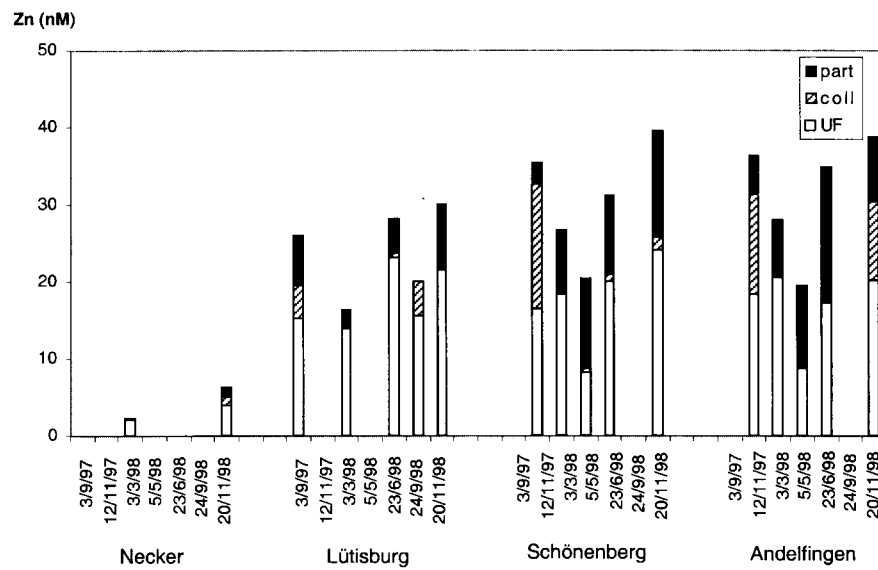


Figure 3b.

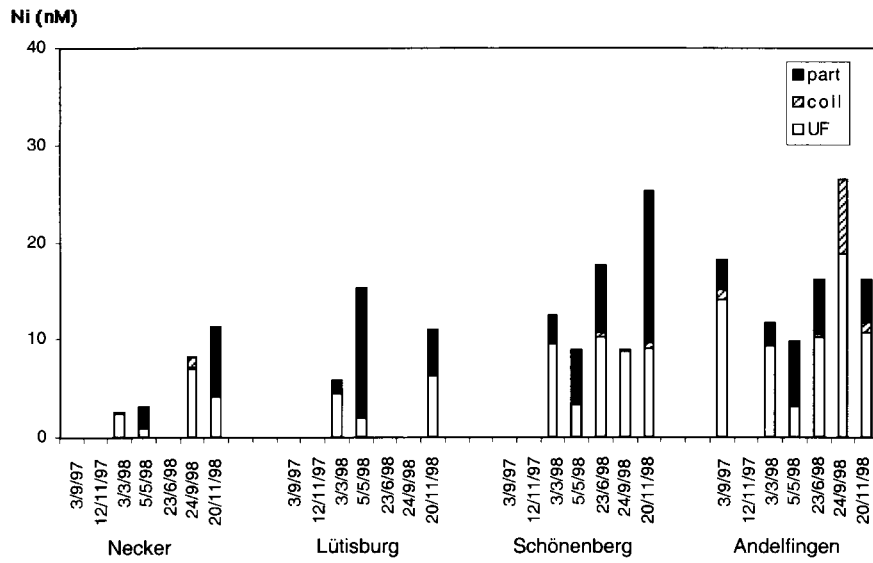


Figure 3c.

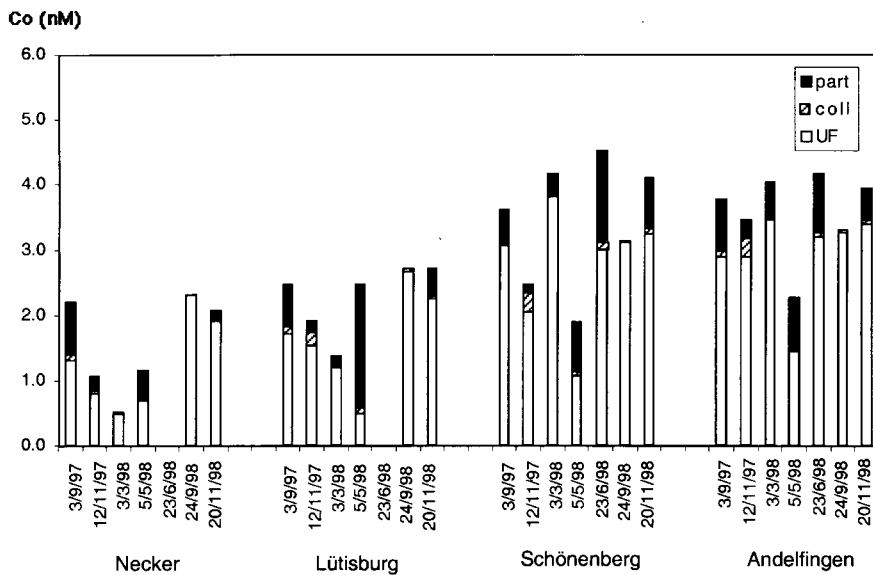


Figure 3d.

typically less than 10% of the $< 0.45\text{-}\mu\text{m}$ filtrate in the colloidal fraction (Figure 3). The percentage of metal in the colloidal fraction, expressed as ratio to the $0.45\mu\text{m}$ -filtrate, thus decreases in the order: Cu (median 11%) > Zn \approx Ni (median 5–6%) > Mn \approx Co (median < 5%).

Dissolved Ca ranges from an average of 1.5 mM at the Necker site to 1.9 mM at the Andelfingen site, Mg from 0.5 to 0.6 mM, alkalinity from 3.5 to 4.5 mM. pH is usually in the range 8.2 to 8.5 at all sites.

The results reported here have all been obtained at low suspended matter concentrations, with typically 1–5 mg L⁻¹ and in few samples up to 10 mg L⁻¹. They indicate the importance of the ultrafiltered fractions for Cu, Zn, Ni and Co under these conditions.

3.3. CU COMPLEXATION IN FILTERED AND ULTRAFILTERED SAMPLES

Titration of the filtered and ultrafiltered samples with Cu and determination of the complexation parameters reveal that strong complexation of Cu occurs both in the 0.45- μ m filtrates and in the ultrafiltrates (Table 2 and Figure 4). Differences in the complexation parameters of filtrates and ultrafiltrates, as indicated by the shifts in the titration curves (Figure 4), are however observed, showing that part of the strong ligands have been removed by ultrafiltration. Out of the total strong ligands in the filtrate, 34–83% (average 71%) are found in the ultrafiltrate at the Necker site and 36 to 74% (average 56%) at the Andelfingen site. The calculated conditional stability constants (pH 8) are very similar in both size fractions at each site (Table 2), but differ among the two sites, with lower log K (13.9 ± 0.4 , all ultrafiltrate and filtrate samples) at the Necker site than at the Andelfingen site (log K = 14.6 ± 0.2). The calculated free Cu²⁺ in Andelfingen are similar to or even lower than those in the Necker, in spite of higher dissolved Cu by a factor of 2–4 in Andelfingen. The ligand concentrations are higher in Andelfingen than at the Necker, in agreement with the increase in DOC.

3.4. RATIOS OF METALS TO ORGANIC CARBON IN ULTRAFILTRATE AND IN COLLOIDS

To compare the relative binding of the trace elements by organic ligands in the ultrafiltrate fraction and in the colloids, the ratios of the metals to organic carbon have been calculated in both fractions (Table 3).

Some accumulation of Cu in the colloids, relatively to organic carbon, is observed at the two upstream sites Necker and Lütisburg, whereas at the downstream sites the Cu/C ratios in the colloids are similar to or lower than those in the ultrafiltrate. These ratios are in agreement with the results of the complexation measurements.

Ni/C ratios in the colloids are in most cases lower than or close to those in the ultrafiltrate, with few exceptions. The trend for Zn is not very clear, with few higher colloidal Zn/C ratios. Co/C ratios in the colloidal fraction are in all cases lower than the Co/C ratios in the ultrafiltrate. These results also indicate that the dissolved species in the range < 10 kD are very relevant for Ni, Zn and Co and that there is no obvious preferential binding of these elements by organic molecules in

Table II. Copper complexation in <0.45- μm filtrates and in ultrafiltrates (UF)

Site		Necker							
Date	Cu (nM)	Cu (nM)	pCu	pCu	L_T (nM)	L_T (nM)	log K	log K	
	<0.45 μm	UF	<0.45 μm	UF	<0.45 μm	UF	<0.45 μm	UF	
12/11/97	4.4	1.3	15.0	15.1	120	41	13.6	13.6	
3/3/98	6.1	5.8	15.0	14.7	119	60	13.8	13.7	
5/5/98	3.2	2.2	15.5	15.0	128	106	13.9	13.3	
23/6/98	7.4	11.0	15.5	15.2	115	147	14.4	14.1	
24/9/98	12.0	10.0	15.2	15.1	118	95	14.3	14.2	
20/11/98	7.1	7.9	15.1	15.2	90	44	14.1	14.5	

Site		Andelfingen							
Date	Cu (nM)	Cu (nM)	pCu	pCu	L_T (nM)	L_T (nM)	log K	log K	
	<0.45 μm	UF	<0.45 μm	UF	<0.45 μm	UF	<0.45 μm	UF	
12/11/97	25.0	23.0	15.4	15.4	260	143	14.5	14.7	
3/3/98	28.0	24.0	15.3	15.1	202	90	14.5	14.7	
5/5/98	10.0	9.1	15.6	15.0	100	60	14.7	14.3	
23/6/98	24.0	21.0	15.3	15.4	191	142	14.5	14.6	
24/9/98	31.0	23.0	15.5	14.9	169	61	14.8	14.6	
20/11/98	23.0	20.0	15.6	15.5	147	97	14.9	15.0	

pCu = $-\log[\text{Cu}^{2+}]$; L_T : ligand concentration.

log K = conditional stability constant (pH 8).

the colloidal range. The low molecular weight species may include complexes with smaller organic molecules and also inorganic species.

3.5. PARTICLE AND COLLOID COMPOSITION; DISTRIBUTION COEFFICIENTS BETWEEN PARTICLES AND SOLUTION

The average composition of suspended particles (measured in the digested particles $> 1 \mu\text{m}$), on a dry weight basis is presented in Table 4A. The composition of the particles with regard to the major elements Ca, Mg, Fe and Mn varies only within a narrow range among the four sites. Ca increases on the average somewhat downstream, whereas Fe rather decreases and Mn slightly increases. Calcium carbonate is an important component of these suspended particles with mostly carbonate rocks in the geochemical background. The few data available for particulate organic C indicate an increase of the fraction of organic matter downstream, which is probably related to inputs from sewage treatment and from agricultural soils.

Table III. Ratios of metals to organic carbon in the ultrafiltrate (Me/DOC UF) and in the colloidal fraction (Me/COC)

Sites	Necker	Necker	Andelf.	Andelf.	Necker	Necker	Andelf.	Andelf.
	Cu/DOC UF	Cu/COC	Cu/DOC UF	Cu/COC	Ni/DOC UF	Ni/COC	Ni/DOC UF	Ni/COC
Date	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)
3/9/97			11.8	5.8			6.1	3.5
12/11/97	1.2	20.7	9.8	11.7				
3/3/98	4.2	3.3	9.8	2.6	2.1	0.0	3.7	0.0
5/5/98	1.5	3.9	4.2	2.4	0.6	0.0	1.4	0.5
23/6/98			10.2	8.9			4.8	2.4
24/9/98	9.9	21.6	13.0	12.0	6.2	21.4	10.4	14.8
20/11/98	9.9	2.7	9.2	36.4	4.2	1.9	4.8	8.5
Sites	Necker	Necker	Andelf.	Andelf.	Andelf.	Andelf.		
	Co/DOC UF	Co/COC	Co/DOC UF	Co/COC	Zn/DOC UF	Zn/COC		
Date	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)	(nmol mgC ⁻¹)		
3/9/97	0.85	0.24	1.25	0.30				
12/11/97	0.77	0.34	1.25	0.54	8.0	23.7		
3/3/98	0.37	0.13	1.38	0.00	8.3	0.0		
5/5/98	0.46	0.00	0.66	0.07	3.9	0.0		
23/6/98			1.52	0.37	8.2	2.3		
24/9/98	2.31	0.00	1.81	0.10				
20/11/98	2.38	0.12	1.54	0.51	9.2	77.6		

UF: ultrafiltrate; COC: colloidal organic carbon.

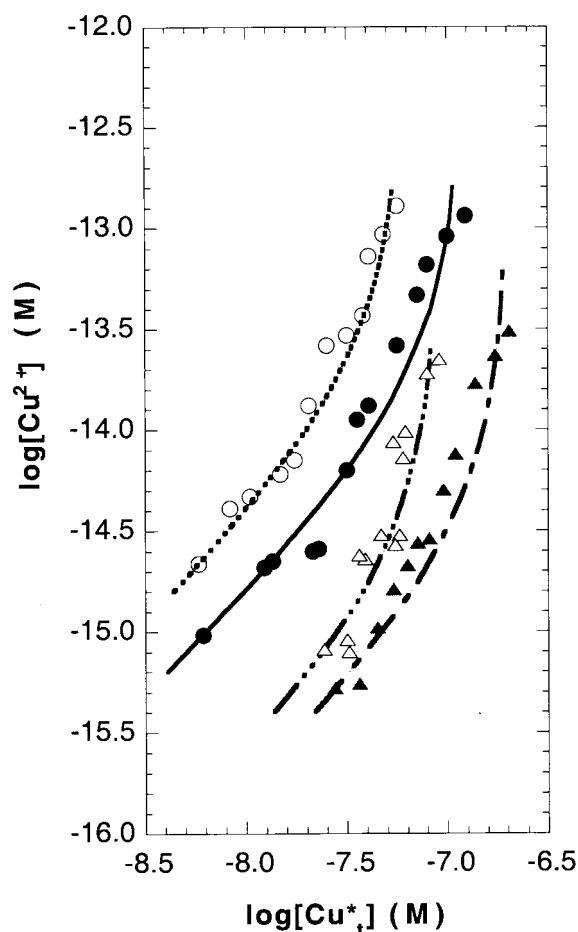


Figure 4. Titration curves of $< 0.45 \mu\text{m}</math>-filtrate and ultrafiltrate samples with Cu ($\log [\text{Cu}^{2+}]$ versus $\log [\text{Cu}_T^*]$ (total added Cu)). Samples are from Necker (black circles for filtrate $< 0.45 \mu\text{m}$ and open circles for ultrafiltrate $< 10 \text{kD}$) and from Andelfingen (black triangles for filtrate $< 0.45 \mu\text{m}$ and open triangles for ultrafiltrate $< 10 \text{kD}$) collected on 4/3/1998. The points are measured and the continuous curves are calculated using the parameters listed in Table 2. A shift of the titration curves to the left indicates less complexation of Cu.$

Slightly higher particle contents of Fe, Co and Ni at the Necker site are probably related to the geochemical background comprising conglomerated rocks. Cu and Zn clearly increase at the downstream sites, whereas no clear trends can be recognized for Ni and Co.

The distribution coefficients ($K_D = \text{Me in particles}/\text{Me dissolved} (\text{L kg}^{-1})$) between the particles and the filtered or the ultrafiltered fraction decrease at the four sites for Cu, Ni and Co, whereas K_D for Zn decreases between the Necker site and the three following sites with similar values (Table 4B). Differences between distribution coefficients based on the $0.45\text{-}\mu\text{m}$ filtered and the ultrafiltered concen-

Table IV. A. Suspended matter composition (particles > 1 μm) (average of 7 samplings, for C, average of 3 samplings)

Sites		Necker	Lütisburg	Schönenberg	Andelfingen
Fe	mmol g ⁻¹	0.44 ± 0.11	0.32 ± 0.05	0.42 ± 0.07	0.35 ± 0.06
Mn	mmol g ⁻¹	0.010 ± 0.003	0.010 ± 0.004	0.013 ± 0.004	0.012 ± 0.003
Cu	$\mu\text{mol g}^{-1}$	0.52 ± 0.32	0.81 ± 0.29	0.73 ± 0.25	0.72 ± 0.35
Zn	$\mu\text{mol g}^{-1}$	1.97 ± 0.91	2.50 ± 0.92	3.25 ± 1.15	2.92 ± 1.01
Ni	$\mu\text{mol g}^{-1}$	1.77 ± 1.09	1.47 ± 0.75	2.10 ± 1.27	1.43 ± 0.69
Co	$\mu\text{mol g}^{-1}$	0.29 ± 0.15	0.16 ± 0.03	0.24 ± 0.11	0.17 ± 0.02
org C	mmol g ⁻¹	1.58 ± 0.46	3.61 ± 0.77	4.31 ± 0.90	4.74 ± 0.96
Ca	mmol g ⁻¹	1.98 ± 0.48	2.55 ± 0.88	2.25 ± 0.80	2.38 ± 0.80
Mg	mmol g ⁻¹	0.59 ± 0.09	0.63 ± 0.19	0.54 ± 0.19	0.59 ± 0.18

B. Partition coefficients between particles (> 1 μm) and ultrafiltrate

Sites		Necker	Lütisburg	Schönenberg	Andelfingen
Cu	log K_D	4.96 ± 0.57	4.84 ± 0.20	4.58 ± 0.21	4.52 ± 0.26
Cu	log $K_D(\text{DOC})$	5.02 ± 0.60	5.03 ± 0.29	4.88 ± 0.18	4.86 ± 0.27
Zn	log K_D	5.80 ± 0.36*	5.19 ± 0.14	5.26 ± 0.32	5.16 ± 0.19
Zn	log $K_D(\text{DOC})$	5.92 ± 0.40*	5.36 ± 0.18	5.56 ± 0.30	5.50 ± 0.18
Ni	log K_D	5.82 ± 0.14	5.34 ± 0.35	5.30 ± 0.24	5.10 ± 0.27
Ni	log $K_D(\text{DOC})$	5.88 ± 0.22	5.52 ± 0.34	5.60 ± 0.20	5.44 ± 0.27
Co	log K_D	5.31 ± 0.28	4.97 ± 0.33	4.94 ± 0.21	4.77 ± 0.14
Co	log $K_D(\text{DOC})$	5.38 ± 0.32	5.15 ± 0.41	5.24 ± 0.18	5.11 ± 0.16

* Zn part/Zn < 0.45 μm .

$K_D = \text{Me particle}/\text{Me UF}$ (L kg^{-1})

$K_D(\text{DOC}) = \text{Me particle}/(\text{Me UF} \times (\text{DOC-UF})^{-1})$ ($\text{L kg}^{-1} \times \text{mgDOC L}^{-1}$)

trations are small for these elements, since the concentration differences between 0.45- μm filtrates and ultrafiltrates are only of the order of 10-30%. The distribution coefficients reflect the downstream increase of the dissolved concentrations, which is only partially coupled to increasing contents in the particle phase (Figure 3 and Table 4).

The influence of the particle composition and of the solution speciation on distribution coefficients was examined by normalizing on one hand the metal content in the particles to Fe, and on the other hand the ultrafiltered metal to ultrafiltered DOC. Normalizing to Fe in the particles takes into account the effect of iron oxides as efficient adsorbing solid phases. This normalization of K_D to Fe does not affect the differences of the distribution coefficients for Cu among the various sites and has only a minor effect on the K_D for Ni, Zn and Co. Normalizing to DOC ($K_D(\text{DOC}) = \text{Me particle}/(\text{Me UF} \times (\text{DOC-UF})^{-1})$, Table 4B) considers that organic ligands tend to maintain metals in solution. Normalizing to DOC strongly

decreases the variability among sites for Cu, and to a lesser extent for Zn, Ni and Co. In both cases, K_D for Zn, Ni and Co are still higher at the Necker site than those at the three other sites. To really take into account the solution speciation, K_D would have to be related to the free ion concentrations.

4. Discussion

4.1. ANTHROPOGENIC AND GEOCHEMICAL FACTORS

The dissolved (both $< 0.45 \mu\text{m}$ and $< 10 \text{ kD}$) concentrations of Cu, Zn, Ni, Co and Mn increase downstream, whereas in the suspended particles only Cu and Zn clearly increase (Figures 2, 3 and Table 4). Trace metal concentrations thus increase downstream, in relation to increasing population density in the catchment and to increasing agricultural soil use. Very low dissolved concentrations of Cu (4–12 nM), Zn (1–6 nM), Ni (1.4–8 nM) and Co (0.7–2.2 nM) are observed at the Necker site, which are assumed to be representative of the geochemical background of the region. The values observed at the Necker site are similar to those that have been determined at other background sites. The Zn concentrations are especially low and similar to values determined, e.g., in various US-rivers (Shiller and Boyle, 1985; Windom et al., 1991) and in Wisconsin rivers (Shafer et al., 1997, 1999). Cu dissolved concentrations at background sites are often observed in the range of 5–10 nM (Benoit et al., 1994; Martin and Windom, 1991; Shafer et al., 1997, 1999; Wen et al., 1999; Windom et al., 1991). The increased concentrations of Cu and Zn downstream are within the range observed in some other systems affected by anthropogenic inputs (e.g., Kraepiel et al., 1997; Martin et al., 1995; Sañudo-Wilhelmy et al., 1996). Much higher concentrations of these elements have been measured in polluted rivers in routine programs, in which often unfiltered samples are collected. The reliability of trace metal data in routine programs has however been questioned (Benoit et al., 1997; Windom et al., 1991).

The observed Ni concentrations are also in the range observed by Kraepiel et al. (1997) in the Gironde estuary (France) and by Wen et al. (1999) in the river end-member of a Texas estuary. Co concentrations in the range of 1 to 6 nM have previously been measured in some Swiss rivers (Qian et al., 1998). An average concentration for Co in river water is given as 1.9 nM (Martin and Windom, 1991).

Significant inputs to the Thur River originate on one hand from agricultural activities and on the other hand from industrial and domestic sewage. These various sources may contribute to Cu and Zn inputs, which appear to contribute more significantly to the dissolved phase. Significant inputs of Cu and Zn from an agricultural area have been recently demonstrated in another region (Xue et al., 2000). Dissolved Ni is likely to originate mostly from industrial inputs. Ni clearly increases at the Schönenberg site, which is located downstream of an industrialized region (e.g., textile industry). The increase of dissolved Mn and Co, which does not correspond to an increase in the suspended particles, is less likely to be directly related to anthropogenic inputs, but may rather be due to changes in the redox

conditions. The increase in Mn in the <10 kD range, which is not accompanied by an obvious increase in the colloidal range, nor in the particulate range, probably indicates the presence of reduced Mn(II). With increasing inputs of organic carbon along the river, the redox conditions in the river bed may be increasingly favorable to the reduction of Mn-oxides and thus to the release of Mn(II). Co may also be released in dissolved form together with Mn(II), since Co is often associated with Mn (Lienemann et al., 1997; Moffett and Ho, 1996).

The increase in filtered Fe may also be linked to Fe-redox cycling, either under reducing conditions in the river bed, or under the influence of light and DOC (Emmenegger, 1999).

4.2. ROLE, NATURE AND ORIGIN OF DISSOLVED LIGANDS AND OF COLLOIDS

The complexation measurements of Cu, as well as the ratios of Cu, Zn and Ni to organic carbon, indicate the importance of organic ligands both in the ultra-filtered and the colloidal fractions for these elements. The decreased variability of distribution coefficients upon normalization to DOC also suggests that binding of Cu, Zn, Ni and Co to dissolved organic ligands has significant effects on their distribution. Detailed investigations of the speciation of these elements in other freshwater systems have indicated significant organic complexation of these elements (Xue et al. 1994, 1996; Qian et al. 1998; Prasad 1999). The colloidal fraction appears to be dominated by organic carbon. It seems thus likely that these metals are mostly bound to organic carbon in the colloids. The preference order of the various elements with respect to binding by colloids corresponds roughly to the order of their binding by humic and fulvic acids. The colloidal fraction is probably mostly of natural origin, including humic acids with molecular weight > 10 kD and mineral particles such as clay minerals.

The results on Cu complexation indicate that the strong ligands consist for a large part of compounds in the < 10 kD range, but that colloidal ligands with similar properties also exist. Furthermore, the ratios of strong ligands to organic carbon in the colloidal fraction (obtained by difference between the 0.45- μ m filtrates and the ultrafiltrates) are higher than the ratios in the ultrafiltrates. Cu is strongly bound by organic ligands at both investigated sites, but the ligands at the Necker site are somewhat weaker. At the Necker site, organic ligands originate mostly from runoff from the soils in the catchment area. They are thus likely to be mostly of the humic and fulvic acid type. These natural ligands may be partly in the < 10 kD range and partly in the > 10 kD range, especially humic acids from soils. At the downstream site Andelfingen, organic ligands may still originate partly from natural soil runoff, but the increase of DOC indicates other sources, namely sewage inputs, inputs from agricultural soils and biotic production in the river itself. The Cu binding ligands originating from these various sources appear to be mostly in the < 10 kD range and to include more specific ligands than at the Necker site, as indicated by the higher complexation constants. These ligands may be of biological origin and may

also include synthetic strong ligands such as EDTA (Nowack et al., 1997; Xue et al., 1993, 1996).

4.3. SIGNIFICANCE OF COLLOIDS IN THE THUR RIVER AND IN OTHER SYSTEMS

The colloidal fraction of trace metals in river water or in river end-members of estuaries has been examined in a number of other studies using similar methods as here (Martin et al., 1995; Sañudo-Wilhelmy et al., 1996; Wen et al., 1996, 1999; Pham and Garnier, 1998; Ross and Sherrell, 1999; Wells et al., 1998). The usual cut-offs for the colloidal fraction are in the range from 1 kD to 10 kD. Variable, but in most cases substantial colloidal fractions of Cu have been obtained in the various studies. Our Cu colloidal fractions are at the low end of the range found in these other studies. The study by Wells et al. (1998) examined in detail the distribution of Cu binding ligands in marine samples in various size classes and showed that about 45% of the strong Cu-binding ligands were > 1 kD and about 12% > 8 kD. Our findings regarding the Cu-ligands show a similar distribution of ligands in the River Thur, with respect to the 10 kD cut-off, with strong ligands distributed over the < 10 kD and > 10 kD size classes.

Ni and Co have been found in several studies to be only to a small extent in the colloidal fraction. Our findings are thus in agreement with these other studies with respect to Ni and Co. The colloidal fractions of Zn and Mn widely vary in various systems. Our results for Zn and Mn are again at the low end of the range found in these other studies. Our findings regarding colloids in the Thur River are thus in broad agreement with other studies in freshwater systems. A similar relative preference of trace elements for binding in the colloidal range has been observed in various studies (Ross and Sherrell, 1999).

Several factors may contribute to the rather low colloidal fractions obtained here for trace metals in the Thur River. The DOC concentrations were rather low, and only 10–20% of DOC were found in the colloidal fraction, in which organic matter appears to be important for binding of trace metals. The suspended matter concentrations at the sampling dates were always in a low range; the colloid concentration may be expected to increase with increasing suspended matter content. The high Ca and Mg concentrations are unfavorable to the stability of colloids in the Thur River and are likely to favor a rapid removal of colloids from the water column. There are no strong redox gradients at which colloidal manganese and iron oxides may be produced. Under high discharge conditions, it is expected that a much larger fraction of the trace elements would be in the particulate size range because of increased amounts of suspended matter. An increase of the colloidal fraction may also be expected in the case of high discharge, but remains to be demonstrated.

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