Aquat.sci. 59 (1997) 176–189
1015-1621/97/020176-14 $ 1.50+0.20/0

Aquatic Sciences

Comparison of Cu and Zn cycling in eutrophic lakes with oxic and anoxic hypolimnion

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Key words: Cu, Zn, Fe and Mn, metal cycling, eutrophic lakes, oxygenated hypolimnion, Lake Sempach, Lake Greifen.

ABSTRACT

Data on the cycling of Cu and Zn in two eutrophic lakes are presented: Lake Greifen that becomes seasonally anoxic in its hypolimnion and Lake Sempach that is aerated during winter and oxygenated during summer. They suggest that hypolimnetic oxygenation 1) enhances the release of copper from the sediment but 2) also accelerates the entrapment and deposition of Cu and Zn by freshly formed Mn- and Fe-oxides.

Introduction

The cycling of copper and zinc in lakes is linked to biological processes, because both elements are essential micronutrients for phytoplankton (Sunda, 1990), as well as to the processes occurring at the oxic-anoxic boundaries (Hamilton-Taylor and Davison, 1995). Binding to biological material leads to the sedimentation of Cu and Zn (Sigg et al., 1987, 1995). However, binding to other types of particles, especially to Fe- and Mn-oxides precipitated within the lakes, may also play a significant role. The redox-driven cycling of Fe and Mn occurring at oxic-anoxic boundaries in many lakes influences the cycling of other elements by scavenging on the surfaces of freshly formed Fe- and Mn-oxides (Hamilton-Taylor and Davison, 1995).

Most studies on the cycling of trace metals in eutrophic lakes have been conducted in lakes with a seasonally anoxic hypolimnion (Morfett et al., 1988; Reynolds and Hamilton-Taylor, 1992; Balistrieri et al., 1992; Sigg et al., 1987, 1995; Hamilton-Taylor and Davison, 1995). In the present study, the sedimentation of Cu and Zn has been investigated in two eutrophic lakes with different redox conditions: Lake Sempach, a eutrophic, but artificially oxygenated lake, offers the opportunity to study trace metal cycling under unique conditions of an oxic hypolimnion, in contact with anoxic sediments, and with high sedimentation rates of organic material and Fe- and Mn-oxides. In comparison, Lake Greifen develops a seasonally anoxic hypolimnion. The comparison between these two lakes allows us to evaluate the relative importance of particle composition (e.g. organic material, Fe and Mn oxide) and of ligands in solution for Cu and Zn sedimentation.

In this study we present data from Lakes Greifen and Sempach on the seasonal variability of Cu and Zn concentrations and speciation in the water column, on the Cu and Zn concentration of settling particles, on the seasonal variability of settling fluxes of these trace metals and on the trace metal concentrations in the sediments. Based on these results we discuss the effects of redox conditions and of hypolimnetic oxygenation on the cycling of Cu and Zn in eutrophic lakes. We are especially interested in examining whether Zn and Cu are recycled from the sediments together with Fe and Mn and whether freshly precipitated Fe and Mn oxides scavenge Zn and Cu and increase their sedimentation rates.

Experimental

Sampling sites

Lake Sempach is a eutrophic lake with an annual primary production rate of about 380 g Cm^{-2} yr^{-1} (Gächter and Meyer, 1990). It is located in cental Switzerland, has a surface area of 14.4 km^2, a volume of 662×10^6 m^3, a maximum depth of 87 m and an average hydraulic residence time of 17 years. Before 1984 the lake was anoxic at depths >60 m during summer; during turnover, mixing was often not intensive enough to completely restore the O_2 deficit. Since 1984, pure oxygen has been introduced into its hypolimnion at a rate of 3 t day^{-1} during summer and during winter it is bubbled with compressed air (370 m^3 h^{-1}) in order to enhance mixing. As a consequence, O_2 concentrations always exceed 3 mg/l, even at the deepest point of the lake (87 m).

Lake Greifen is highly eutrophic with an annual primary production rate of 500 g Cm^{-2} yr^{-1} (Bührer and Wasmer, 1992). It has a surface area of 8.5 km^2, a volume of 150×10^6 m^3, a maximum depth of 32.2 m, and an average hydraulic residence time of 1.1 year. From June to November, the lake is anoxic at depths exceeding 10 m.

Collection of settling particles

Sediment traps (Plexiglas tubes with a height-to-diameter ratio of 9 to 10) were exposed at the deepest locations of both lakes at depths of 15 m and 28 m in Lake Greifen (Kuhn, 1992) and of 20 m and 80 m in Lake Sempach, respectively. The settling material was collected at approximately 3 weeks intervals (2–5 weeks) during the year 1990/91 in both lakes and during 1994 in Lake Sempach. It was freeze-dried, weighed and kept at low temperature (4 °C) until analysis.

Undisturbed sediment cores (diameter 6.5 cm) were collected at the deepest location, in Jan. 1994 and Oct. 1995 in Lake Sempach, and in Dec. 1995 in Lake Greifen, respectively. After sampling, the sediment cores were sliced in 0.5–1 cm thick layers within 4 h after collection. They were then freeze-dried, weighed and kept at 4 °C till analysis.

Analysis of sediment-trap material and sediment cores

For metal analysis, the freeze-dried material was digested with HCl-HNO_3 in a microwave digestion device (Milestone MLS-1200 Mega) at high pressure (up to 8 bars) for 2 hours in Teflon beakers, cleaned with HNO_3 (Sigg et al., 1995). Fe, Mn, Ca, Mg, Zn and Cu were determined by inductive coupled plasma optical emission spectrometry (ICP-OES). Particulate phosphorus was determined by the molybdate spectrophotometric method (Standard methods, 1989), after digesting the dry material by HCl-HNO_3 in a microwave digestion device or by $K_2S_2O_8$ in an autoclave at 120 °C for 2 hours (Gächter et al., 1992). The results from the two digestion techniques agreed within about 10%. Organic C and N were determined by a C, H, N analyzer (Heraeus) on Whatman GF/F filters according to Hupfer et al. (1995).

Metal concentrations in the water column

Water samples were collected in depth profiles at various times of the year at the deepest locations of both lakes, using a Go-Flo sampler (General Oceanics, 5L), that had been carefully cleaned with HNO_3. Within a few hours after sampling, samples were filtered in the laboratory (pore size 0.45 μm), dry weight of suspended solids was determined and samples for determination of dissolved metals were acidified to 0.01 M HNO_3. All bottles and filters were carefully cleaned with 0.01 M HNO_3.

Dissolved Zn was determined in acidified filtered samples by flame atomic absorption spectromery (AAS) after preconcentration; the reproducibility of this method is about 5–10% (Sigg et al., 1996). The limit of determination is about 3 nM. Dissolved copper was determined in acidified filtered samples using AAS with direct injection into the graphite furnace. The limit of determination is 3 nM for Cu. In some of the samples Zn and Cu were determined by inductive coupled plasma mass spectrometry (ICP-MS, ELAN 5000, Perkin-Elmer Sciex). Zn and Cu determinations by AAS agreed well with direct measurements conducted by ICP-MS. Dissolved Fe, Mn, Ca and Mg were determined by ICP-OES.

Trace metal speciation in the water column

To investigate the effects of dissolved ligands on sedimentation of trace metals, copper complexation by ligands in solution was evaluated by ligand exchange with catechol and subsequent differential pulse cathodic stripping voltammetry (DPCSV) of the copper-catechol complexes (Xue and Sigg, 1993). The filtered water samples were kept in polyethylene bottles in the dark at 4 °C until analysis, which was performed within 1–3 days after sampling. The free aquo Cu^{2+} concentration at ambient dissolved copper concentration was calculated from the concentration of copper-catechol complexes formed by ligand-exchange equilibrium and determined by DPCSV. Titration curves with Cu were obtained by spiking aliquots of lakewater samples with different Cu concentrations. The free aquo

Zn^{2+} concentration (Zn^{2+}) was evaluated by ligand exchange with EDTA (ethylenediaminetetraacetic acid) and anodic stripping voltammetry (ASV) of the labile zinc (Xue and Sigg, 1994). Labile and non-labile Zn species were distinguished by DPASV. The ZnEDTA complex is non-labile. The decrease in labile Zn concentration was measured as a function of added EDTA, and $[Zn^{2+}]$ was calculated from ZnEDTA formed in equilibrium with the natural ligands in solution.

Results

Cu and Zn in the water column

The general composition of the lake water with respect to major ions and to dissolved organic carbon (DOC) is quite similar in these two lakes (Lake Greifen: Ca $1.2–1.5 \times 10^{-3}$ M, Mg 0.6×10^{-3} M, alkalinity $3–4 \times 10^{-3}$ M, pH 7.5–8.5, DOC 3–4 mg/L; Lake Sempach: Ca $0.5–1.2 \times 10^{-3}$ M, Mg 0.3×10^{-3} M, alkalinity $1.5–2.5 \times 10^{-3}$ M, pH 7.5–9, DOC 2.8–4.5 mg/L).

Concentrations of dissolved Zn and Cu are in both lakes in the nanomolar range, with two to threefold higher concentrations in Lake Greifen (Fig. 1). Total Zn and Cu concentrations did not significantly differ from the dissolved metal concentrations in either of the two lakes, because the particle concentrations are lower than 4 mg/L in the whole water column. Seasonal variations of dissolved Zn and Cu were observed in both lakes, with typically a decrease of dissolved Zn and an increase of dissolved Cu between winter overturn and summer stagnation (Fig. 1). In Lake

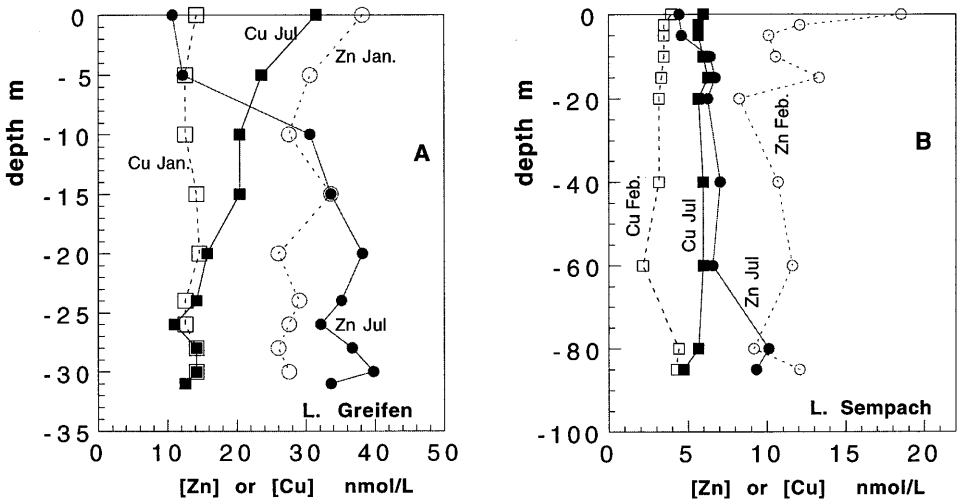

Figure 1. Vertical profiles of dissolved Cu and Zn concentrations in the water columns of Lake Greifen and Lake Sempach. The samples from Lake Greifen were collected on 11 July and 9 January 1990 (A), those from Lake Sempach on 18 July and 28 February 1994 (B)

Greifen, differences between epilimnion and hypolimnion are apparent; Zn decreased in the epilimnion during summer stagnation, whereas Cu increased. In Lake Sempach, the depth dependence is less clear, but Zn decreased and Cu increased in the whole water column during summer stagnation.

The speciation of Cu and Zn gave similar results in both lakes. Cu was very strongly complexed by dissolved organic ligands, with ratios of $[Cu^{2+}]$ to dissolved Cu of about $1-2 \times 10^{-7}$. pCu ($= -\log [Cu^{2+}]$) was similar in the epilimnion of both lakes: pCu = 14.8 (±0.4, n = 11) in Lake Greifen and 15.0 (±0.3, n = 4) in Lake Sempach. Differences in complexation between epilimnetic and hypolimnetic samples were observed only in Lake Sempach, but not in Lake Greifen.

In contrast to Cu, a substantial fraction of Zn was present as free zinc Zn^{2+} and as weak organic complexes in samples from both lakes; 3–15% of total dissolved Zn were evaluated to be free Zn^{2+} (Xue et al., 1995). Average epilimnic $[Zn^{2+}]$ were 1.7×10^{-9} M in Lake Greifen and 7.1×10^{-10} M in Lake Sempach, respectively.

The molar ratio of dissolved Zn to dissolved Cu was 2–4 in both lakes during overturn and 0.4–1 during summer in the epilimnion. In contrast, the concentrations of the free ions differed by several orders of magnitude, with ratios $[Zn^{2+}]:[Cu^{2+}] = 2 \times 10^5 - 10^6$ in Lake Greifen and $2 \times 10^4 - 10^6$ in Lake Sempach.

Iron and manganese in the water column

In both lakes Mn accumulated in the hypolimnion during summer (Fig. 2); in Lake Sempach this accumulation is mostly limited to the deepest layers. In a similar way as observed for Cu, “dissolved” (<0.45 μm) Fe increased throughout the water column between January and July in Lake Sempach. No such accumulation was observed, however, in Lake Greifen, where strongly reducing conditions likely permitted the formation of highly insoluble FeS.

Composition of settling particles and sedimentation rates of Zn and Cu

Table 1 gives the yearly sedimentation rates and Table 2 lists the yearly average of the chemical composition of the settling particles collected by sediment traps in Lake Greifen and Sempach. Seasonal variations in the sedimentation rates of several elements are shown in Figure 3.

In Lake Greifen, the 15 and 28 m traps were both located within the anoxic hypolimnion during summer stagnation. Average composition, as well as the average sedimentation rates were very similar at both depths in Lake Greifen. The sedimentation rates of Fe, Mn, P and Zn differed only during a short period of the yearly cycling (in spring, May–June, Fig. 3). Lake Sempach is much deeper, and the traps are therefore much farther apart (20 m and 80 m depth). There were clear differences in the composition, as well as the sedimentation rates between both traps in Lake Sempach (Table 1, 2, Fig. 3). Mn and Fe fluxes measured at 80 m exceeded those observed at 20 m depth practically throughout the year and so did the trace metal fluxes (Fig. 3B).

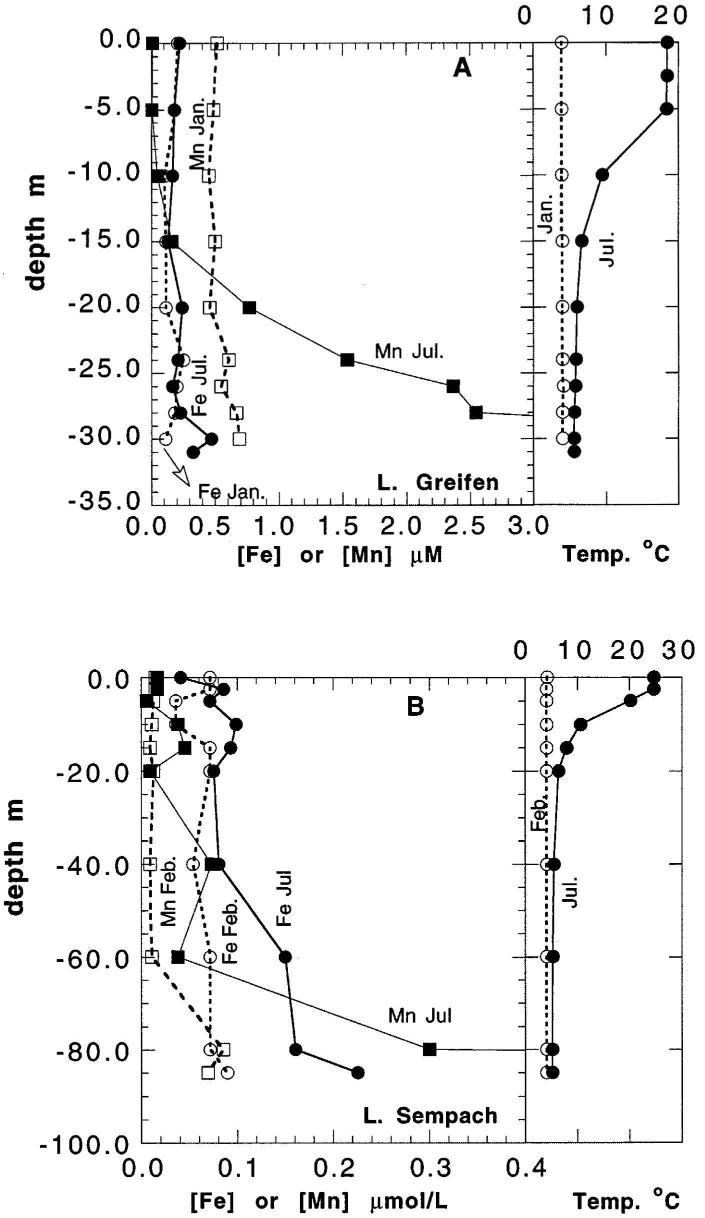

Figure 2a, b. Vertical profiles of dissolved (< 0.45 μm) Mn and Fe concentrations, and temperatures in the water columns of Lake Greifen and Lake Sempach. The samples from Lake Greifen were collected on 11 July and 9 January 1990 (A), those from Lake Sempach on 18 July and 28 February 1994 (B)

Table 1. Yearly sedimentation rates* in Lakes Sempach and Greifen (1990)

Element		Lake Greifen 15 m trap	Greifen 28 m trap	Sempach 20 m trap	Sempach 80 m trap
Total	$g \cdot m^{-2} \cdot d^{-1}$	2.87	2.75	1.45	1.84
C	$mg \cdot m^{-2} \cdot d^{-1}$	224.1	202.4	109.1	160.9
N	$mg \cdot m^{-2} \cdot d^{-1}$	31.4	30.8	19.4	28.1
P	$mg \cdot m^{-2} \cdot d^{-1}$	6.64	6.67	4.06	7.81
Fe	$mg \cdot m^{-2} \cdot d^{-1}$	12.7	15.5	13.0	27.8
Mn	$mg \cdot m^{-2} \cdot d^{-1}$	11.2	14.0	4.7	30.8
Zn	$\mu g \cdot m^{-2} \cdot d^{-1}$	330	340	180	270
Cu	$\mu g \cdot m^{-2} \cdot d^{-1}$	68	74	80	151

* Multiply all the figures with 365 to obtain the yearly sedimentation rates.

Table 2. Yearly average element composition[a] of settling materials and sediments collected in Lakes Greifen and Sempach

		Lake Greifen	Lake Greifen	Lake Sempach	Lake Sempach
Settling material		15 m trap	28 m trap	20 m trap	80 m trap
C	mg/g DW	78.1	73.6	75.2	87.4
N	mg/g DW	10.9	11.2	13.4	15.3
P	mg/g DW	2.3	2.4	2.8	4.2
Fe	mg/g DW	4.4	5.6	9.0	15.1
Mn	mg/g DW	3.9	5.9	3.2	16.7
Zn	µg/g DW	115	124	124	147
Cu	µg/g DW	23.7	26.9	55.2	82.1
Sediment core		0–2 cm[b]	2–6 cm[b]	0–2 cm[c]	2–6 cm[c]
Fe	mg/g DW	9.6 ± 2.6	13.0 ± 1.7	16.6 ± 6.0	15.5 ± 1.6
Mn	mg/g DW	0.5 ± 0.1	0.7 ± 0.0	2.8 ± 1.9	2.0 ± 0.4
Zn	µg/g DW	99.3 ± 17.0	111.8 ± 6.3	125.8 ± 27.2	142.6 ± 26.7
Cu	µg/g DW	31.0 ± 7.0	32.0 ± 1.8	47.3 ± 6.8	44.0 ± 6.9

[a] Yearly average in 1990, obtained from yearly elemental sedimentation rate divided by yearly total sedimentation rates.
[b] Average over 1 core, 4 slices.
[c] Average over 2 cores, 4 slices in each.

Due to lower algal productivity, lower sedimentation rates of total dry material, organic C, N, P, Ca and Mg were observed in Lake Sempach than in Lake Greifen (Table 1). The hypolimnetic Fe, Mn and Cu sedimentation rates observed in Lake Sempach exceeded the ones observed in Lake Greifen about twofold.

The organic C and N contents of the settling particles were similar in both lakes, indicating a similar fraction of biogenic material (Table 2). With respect to P, Mn, Fe and Cu, the composition of the settling particles differed however between the two lakes. Clear differences were observed in particular between the particles from the deeper trap (80 m) in Lake Sempach and those from Lake

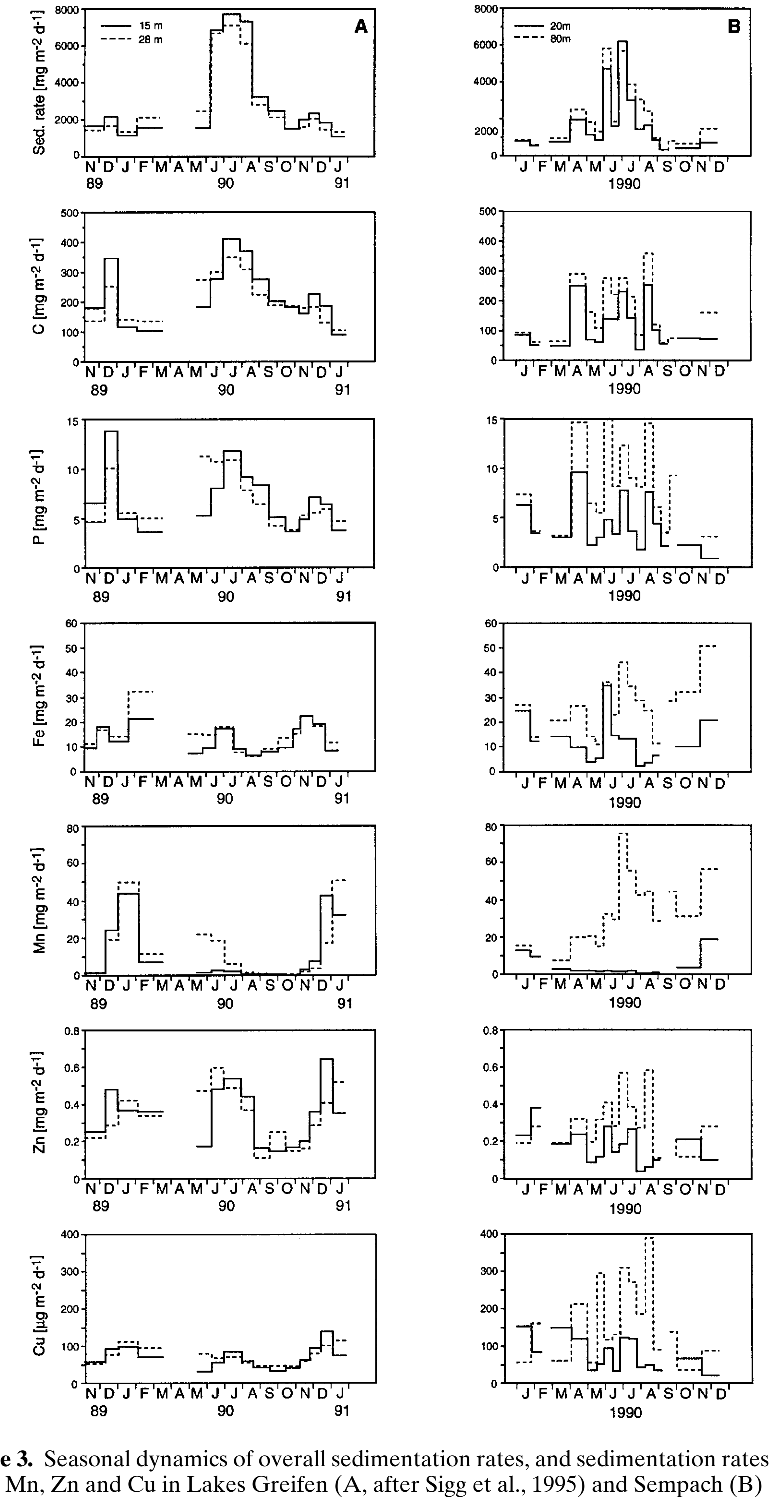

Figure 3. Seasonal dynamics of overall sedimentation rates, and sedimentation rates of organic C, P, Fe, Mn, Zn and Cu in Lakes Greifen (A, after Sigg et al., 1995) and Sempach (B)

Greifen. The P, Fe, Mn and Cu contents of the particles collected in the bottom trap of Lake Sempach were much higher than those of particles collected at 20 m or at both depths in Lake Greifen. However, the Zn concentrations of the settling particles were similar in both lakes, and only about 20 % higher in the lower trap of Lake Sempach (Table 2).

As indicted in Table 2, the yearly average copper concentration of settling particles collected above the lake bottom in Lake Sempach exceeded that of the sediment clearly (82 µg Cu/g dry weight compared to 44 to 47 µg Cu/g dry weight), suggesting some diagenetic release of Cu at the deepest location of Lake Sempach. In contrast, the concentrations in the settling material of Zn in both lakes and of Cu in Lake Greifen were close to those observed in the sediments. Therefore, no release from hypolimnetic sediments can be inferred for Cu in Lake Greifen, nor for Zn in both lakes.

Discussion

Surprisingly the yearly average Cu concentration of the settling particles as well as the particulate Cu flux to the sediment were larger in Lake Sempach than in Lake Greifen, although in the water column the Cu concentration in Lake Greifen exceeded that in Lake Sempach at least twofold. Zn concentrations of settling particles were about equal in both lakes although the Zn concentration in the water column was three times higher in Lake Greifen than in Lake Sempach. If these results are expressed in terms of distribution coefficients between solid particles and solution, the distribution coefficients both of copper and zinc were higher in Lake Sempach, although pH and DOC are quite similar. These results suggest a more efficient binding of trace metals to the settling material in Lake Sempach that is probably related to the composition of the particles, and therefore a more efficient elimination of the metals from the water column.

In both lakes the dissolved Cu concentration increased between overturn and early summer. In Lake Greifen this increase was restricted to the uppermost 20 m and may be due to the inputs from tributaries into the epilimnion, combined with the relatively low Cu sedimentation rate during summer, or alternatively to release from sediment overlaid with oxic water in the shallow parts of the lake. In Lake Sempach, the increase of dissolved Cu down to a depth of 80 m is more likely to be due to release from sediments than to external sources, because during stagnation inputs into the epilimnion would not mix down easily. The similarity of the depth profiles of Fe and Cu also indicates a common origin of increased Cu and Fe; no clear increase of Cu was however observed close to the sediment, probably because of the counteracting effects of release of Cu and redeposition together with the Fe- and Mn-oxides.

The comparison of the yearly average Cu concentration of the settling particles with the average Cu concentration of the sediments, as well as the comparison of the sedimentation rates at different depths suggest some release of Cu from the sediment of the permanently oxic Lake Sempach, but no release from the sediment of the transiently anoxic Lake Greifen. If the increase in Cu concentration observed between February and July in Lake Sempach (Fig. 1) was due to release from sediments, then the average release rate was about 55 µg Cu m^{-2} day^{-1}. A comparison of the Cu concentration, in Table 2, of the settling material (82 µg Cu/g DW) and the concentration of the sediment (about 45 µg Cu/g DW) suggests that on a yearly average about half of the settled Cu was released again. Since average gross sedimentation was 151 µg Cu m^{-2} day^{-1} (Table 1), the estimated release is 76 µg Cu m^{-2} day^{-1}. Hence, the two independent estimations of Cu release from the sediment of Lake Sempach agree well, and the observed increase in Cu concentration could well be explained by release of Cu from sediments overlaid with oxic water.

The two lakes differ mainly in the oxygen content of their hypolimnia. Whereas the hypolimnion of Lake Greifen becomes increasingly anoxic early in summer, that of Lake Sempach is artificially maintained oxic throughout the year. Oxic conditions accelerate the mineralization of the organic material, to which Cu may be bound. Oxic conditions at the sediment surface may therefore accelerate the release of Cu from the organic material reaching the sediment. Kerner and Geisler (1995) have demonstrated this release of Cu into overlying water during early aerobic degradation in the laboratory.

According to Fig. 1, no net release of Cu was observed in the hypolimnion of Lake Greifen between January and July. This agrees well with the observation that copper concentrations of the settling material (27 µg/g DW) and of the sediment (30 µg/g DW), see Table 1, were about equal. The results also agree well with the hypothesis that oxic conditions favour the release of Cu from the sediment due to increased mineralization velocity of the organic material.

In Lake Greifen, in which the hypolimnion is anoxic during summer, reduced Mn, and only to a small extent Fe, accumulate in the lower hypolimnion (Fig. 2). Fe and Mn are only reoxidized and reprecipitated during the next overturn, and then will scavenge Cu and redeposit is homogeneously distributed all over the lake bottom. In Lake Greifen, Mn(II) is present throughout the anoxic hypolimnion (up to about 10 m depth) during summer stagnation. The sedimentation rates of Fe, Mn, Cu and Zn increased, however, from October to December, even in the 15 m trap due to the reoxidation of Mn(II) (Fig. 3). In contrast, in the oxygenated hypolimnion of Lake Sempach, the released Fe and Mn are permanently reoxidized close to the sediment surface (Wehrli et al., 1995). Very likely, Cu released from the sediment is subsequently redeposited, in association with these freshly precipitated Fe- and Mn-oxides. During overturn and early summer, Cu concentrations might have increased in the whole aerobic water column of Lake Sempach, because more Cu was released from the sediment than returned to it by sedimentation.

Contrary to Cu, the Zn concentrations decreased from February to July throughout the water column in Lake Sempach and in the upper water layers of Lake Greifen. Zn may be released from organic material together with Cu, but be less mobile than Cu at the sediment-water interface, due to its much smaller affinity to organic ligands. The decrease of Zn in the epililmnion of Lake Greifen from January to July is attributed to uptake by algae and subsequent sedimentation (Sigg et al., 1996). In addition to the Zn removal by algae, the more efficient removal of Zn by reoxidized Mn and Fe in the hypolimnion of Lake Sempach might explain why in this lake Zn concentration decreased throughout the water column and not only in the epilimnion as observed in Lake Greifen (Fig. 1).

Comparison of the seasonal dynamics of the fluxes gives some insights into the relative importance of organic material, Fe and Mn oxides as scavengers for trace metals. Fig. 3A shows that in Lake Greifen trace metal fluxes peaked simultaneously with the flux of organic material during summer, whereas during winter, trace metal fluxes peaked when Mn and Fe did so. In a similar way, the observed increases in trace metal sedimentation in the oxygenated hypolimnion of Lake Sempach might be related to the enhanced cycling of Fe and Mn in this lake. As shown by the multiple correlations given by equations (1) and (2), the differences in Cu or Zn fluxes between hypolimnion and epilimnion can be well attributed to the differences of Fe and Mn fluxes between the hypolimnion and epilimnion of Lake Sempach:

$$\Delta F_{Cu} = 2.01 \times 10^{-3} \times \Delta F_{Mn} + 3.85 \times 10^{-3} \times \Delta F_{Fe} \text{ (n = 22, r = 0.71)} \tag{1}$$

$$\Delta F_{Zn} = 5.28 \times 10^{-4} \times \Delta F_{Mn} + 9.28 \times 10^{-3} \times \Delta F_{Fe} \text{ (n = 23, r = 0.71)} \tag{2}$$

where ΔF_i represents the difference in fluxes of component i between two depths in mg m^{-2} d^{-1}.

Freshly precipitated Fe(III) hydroxides and Mn(III/IV) oxides are known to have large surface areas with a high number of binding sites for metals. For example, maximum adsorption capacities for trace metals on amorphous Fe(III)-hydroxide have been found to be 2×10^{-3} mol/g for $Fe(OH)_3$ (Dzombak and Morel, 1990)) and 1.8×10^{-3} mol/g MnO_2 for natural manganese oxide (Mason, 1996). These high adsorption capacities suggest that the Fe(III) and Mn(IV) oxides represent a large fraction of the available functional groups in the settling particles. Therefore, they may play an important role in binding Cu and Zn, although Fe and Mn represent only a small fraction of the settling material in terms of dry weight. In Lake Sempach, Mn and Fe oxides were relatively more important than in Lake Greifen. Binding to these oxides may hence partly be responsible for the higher solid/solution distribution coefficients for Zn and Cu in this lake. In a simple approach, binding by strong organic ligands is expected to compete with binding to the surfaces of Fe- and Mn-oxides. Taking into account the measured speciation in solution, Zn could be easily bound to these oxides, because it is not strongly complexed. A simple equilibrium calculation of binding of Cu to a Fe-oxide surface in competition with the strong complexation by organic ligands leads to the conclusion that Cu could hardly be bound directly to the metal oxide surface (Sigg et al., 1995). Additional mechanisms have therefore to be involved. Ternary complexes including organic ligands, surface groups and metal ions may contribute to strong binding of Cu and Zn to oxide surfaces. The formation of ternary complexes and the occurrence of polymeric species of metal ions with mineral surfaces and organic ligands have been demonstrated by experiments and modelling (Davis, 1984; Schindler, 1990; Buffle et al., 1995).

From the available data on the two lakes, there is qualitative evidence for increased cycling of Cu between sediment and water column under conditions of artificial oxygenation. It is however not clear whether these conditions result in increased Cu concentrations, because the effets of more efficient binding to the settling particles and of enhanced release from the sediment are counteracting each other.

With regard to the overall mass balance in the lake, the lower Cu and Zn concentrations in the water column of Lake Sempach, in comparison to Lake Greifen, could also be related to lower concentrations in the tributaries and to the effect of the longer water residence time. Information on the concentrations in the tributaries of both lakes would be needed to evaluate quantitatively whether artificial oxygenation of eutrophic lakes enhances or diminishes overall trace metal elimination.

Conclusions

The comparison of the metal cycling in Lakes Greifen and Sempach suggests that hypolimnetic oxygenation enhances the release of copper from the sediment. In the case of Lake Sempach, Cu may be released during aerobic degradation of organic matter and be relatively mobile, probably still bound in small organic complexes (Fig. 4). It then becomes adsorbed to the Fe and Mn oxides and is redeposited at the sediment surface. In the case of Lake Greifen, the degradation of organic matter is slower at the anoxic sediment-water interface. Cu released from organic material might be retained in the sediments, possibly as sulfide or adsorbed to iron sulfide (e.g. Huerta-Diaz et al., 1993).

Artificial oxygenation prevents the development of an anoxic hypolimnion and hence a seasonal accumulation of reduced Fe and Mn and of trace metals. It accelerates the cycling of Fe and Mn between the sediment and the water column in the immediate vicinity of the sediment/water interface. It has been shown in another lake with similar conditions (Lake Baldegg) that, as a consequence, artificial oxygenation leads to a geochemical focusing effect (Schaller and Wehrli, 1997; Schaller et al., 1997). The reoxidation of released Mn(II) and Fe(II) is the most efficient where oxic water meets water enriched with reduced Fe(II) and Mn(II). Such conditions are mainly met where the plane of the oxycline cuts the sediment surface. Because in a stratified lake horizontal mixing exceeds vertical mixing by some orders of magnitude, released Fe(II) and Mn(II) are quickly horizontally mixed and therefore tend to settle after oxidation, not at the location of their releases, but more towards the center of the lake (Schaller and Wehrli, 1997). It is likely that a similar focusing effect is occurring in Lake Sempach. Our data show that the reduction of Fe and Mn in the sediment and their rapid reoxidation close to the sediment/water interface resulted in an enrichment of the settling particles not only with Fe and Mn, but also with elements such as P (Hupfer et al., 1995), Cu and Zn. This redox driven movement may therefore also result in a lateral focusing of these trace elements towards the deepest point of the lake. Spatially distributed data on these trace elements in sediment would be necessary to test this hypothesis. In Lake Greifen, in contrast, the reoxidation of Mn(II) occurred only during complete overturn. In this case, such focussing is not likely to occur, because under well mixed conditions the newly formed flocs tend to settle evenly distributed over the total sediment surface.

ACKNOWLEDGEMENTS

We are indebted to David Kistler, Erwin Grieder and Antonin Mares for their help in sampling and chemical analysis and grateful to Annette Kuhn for her sediment trap data from L. Greifen.

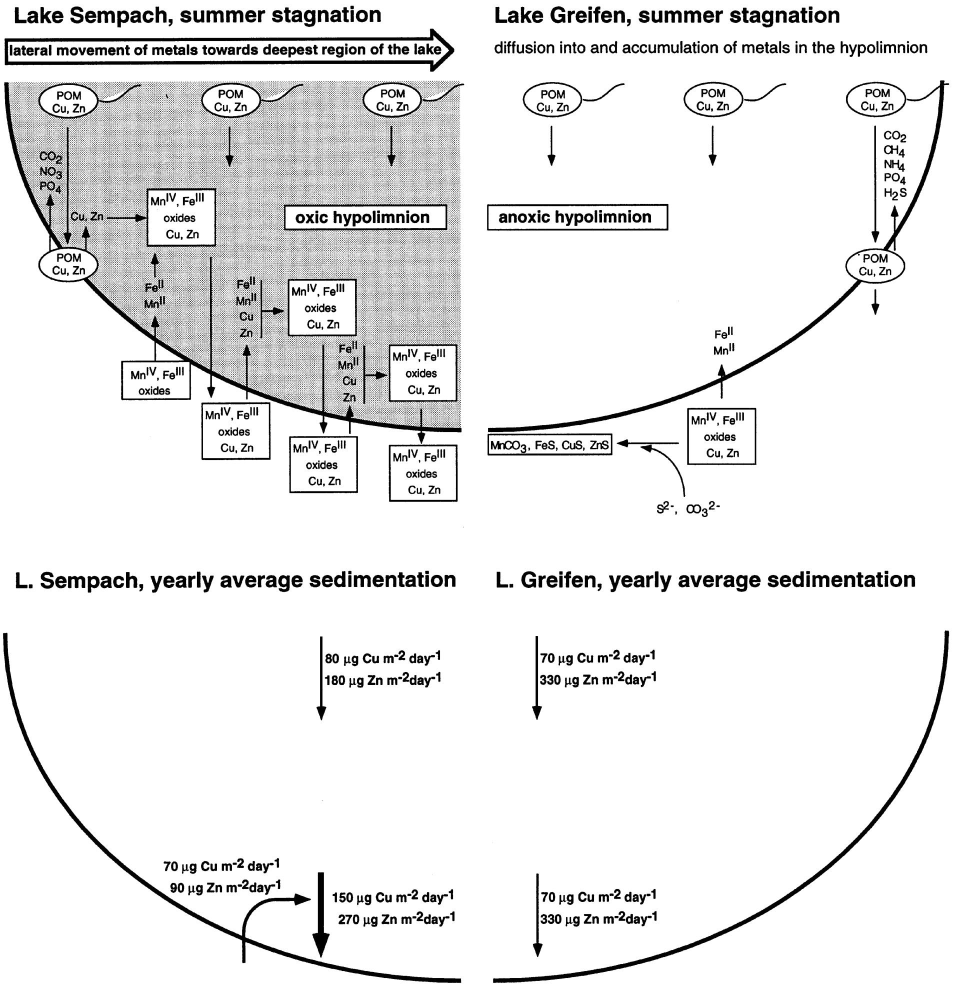

Figure 4. Sketch of Cu and Zn cycling in Lakes Sempach and Greifen

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Received 10 June 1996;
revised manuscript accepted 22 January 1997.