Seasonal Variations of Zinc in a Eutrophic Lake

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Abstract. Depth profiles of dissolved zinc were measured monthly over one year in Lake Greifen, a eutrophic lake. The concentrations are in the range 10–40 nM and show systematic variations over time and depth. Due to the increased binding to particles and subsequent settling, concentrations of zinc in the epilimnion decrease during summer stagnation. Clear correlations between Zn and major nutrients (P, Si) are, however, not observed in the water column. No accumulation of Zn occurs in the anoxic hypolimnion. The Zn sedimentation is related to the sedimentation of algae and of manganese oxide. A mass-balance calculation shows that 87% of the Zn input is retained in the sediments of Lake Greifen.

Key words: zinc, eutrophic lake, sedimentation, mass-balance, model, trace elements, depth profiles

1. Introduction

Zinc, as an essential element, is involved in the biological cycles in lakes, due to its uptake by algae. Zinc in natural waters is also highly influenced by anthropogenic sources, due to its wide use. Anthropogenic Zn inputs to freshwater are in many cases high in comparison to the natural inputs; domestic and industrial waste waters, as well as atmospheric depositions, are loaded with Zn. Interactions of trace elements with phytoplankton have received much attention in the oceans, in which the concentrations of certain trace elements may be growth-limiting (Bruland, 1983; Bruland *et al.*, 1991; Morel *et al.*, 1991). The vertical distribution of many trace elements in the oceans has been carefully determined (Bruland, 1983; Whitfield and Turner, 1987) and provides insight into the predominant processes. Relationships between various trace elements and nutrients have been demonstrated from these studies, indicating the influence of biological processes on the distribution of trace elements in the oceans. Stoichiometric ratios of trace elements to major nutrients (P, Si) have been derived from these correlations, which are expected to be characteristic of algal material in a similar way as the ratios of the major nutrients C : N : P (Bruland *et al.*, 1991; Morel *et al.*, 1991). Correlations of Zn with dissolved silicate, as a major nutrient, have been found in depth profiles of the oceans (Bruland, 1980).

Uptake and release by phytoplankton are expected to affect the distribution of trace elements in lakes (Sigg, 1985; Murray, 1987). In an ideal case, in which phytoplankton plays the most significant role for the distribution of Zn or of

other trace elements, correlations of Zn with major nutrients should be observed in the water column of lakes in a similar way as in the oceans. Various other factors, which are not very significant in the oceans, may however play a role in lakes. Namely, there may be high and variable local inputs of trace elements; transport by nonbiological particles may be significant; the mixing processes in lakes undergo seasonal variations; anoxic conditions are encountered in the deeper part of eutrophic lakes. Furthermore, the Zn concentrations in many lakes may be increased by various sources and may therefore be much higher than the limiting range as a micronutrient for phytoplankton.

Few studies on the distribution of Zn in the water column of lakes are available (Baccini and Joller, 1981; Morfett *et al.*, 1988; Balistrieri *et al.*, 1992; Reynolds and Hamilton-Taylor, 1992; Tessier, 1989). The study of Zn in Lake Windermere during a diatom bloom (Reynolds and Hamilton-Taylor, 1992) points to the importance of Zn uptake by algae. Data from Lake Sammamish (Balistrieri *et al.*, 1992) also indicate the role of biological cycling of Zn. Ratios of Zn to silicate and phosphate were derived from concentrations in the water column, both in the case of Lake Windermere and of Lake Sammamish.

In the present study, we consider the seasonal variations of zinc in the water column of a eutrophic lake (Lake Greifen, Switzerland), and attempt to relate these variations to the uptake and release of major nutrients by phytoplankton and to the sedimentation processes. We examine whether the role of Zn as an essential micronutrient can be demonstrated in the water column, and whether ratios of Zn to major nutrients can be derived. The role of anoxic conditions in the hypolimnion during a significant part of the year is also assessed with regard to the distribution of Zn in the lake. A mass-balance calculation is performed, in which the data in the water column and the sedimentation rates are combined.

2. Experimental Section

2.1. LAKE DESCRIPTION

Lake Greifen is a small eutrophic lake on the Swiss Plateau; it is located in a densely populated area and receives high nutrient inputs from sewage and agricultural runoff. The surface area of Lake Greifen is $8.5 \times 10^6 \text{ m}^2$ and its volume is $150 \times 10^6 \text{ m}^3$; its average depth is 17.7 m, with a maximum of 32.2 m. The residence time of water is 1.1 years. Thermal stratification lasts approximately from May to December, and lake overturn usually takes place in December–January. An anoxic hypolimnion develops during summer stagnation approximately from June to December. Monthly samplings were performed at the deepest point of the water column (depth = 31 m) over a period of two years (January 1989–January 1991).

2.2. SAMPLING AND FILTRATION

Water samples were collected in Go-Flo samplers (General Oceanics), which had been cleaned by soaking in HNO_3 and nanopure water (Nanopure, Barnstead) and rinsed with lake water at the beginning of the sampling. In order to avoid contact of the anoxic samples with oxygen, the samples were transferred from the Go-Flo samplers into bottles equipped with three-way taps under N_2 pressure. These bottles had been previously flushed with N_2 and were completely filled. Filtration in the laboratory with acid-cleaned $0.45\ \mu\text{m}$ cellulose nitrate filters (Sartorius) and a polycarbonate filtration unit (Sartorius) was also carried out under N_2 gas in a closed system, avoiding contact of the samples with laboratory air. Filtered samples for Zn determination were immediately acidified to $\text{pH} \approx 2$ with HCl (concentrated, suprapure, Merck).

2.3. SEDIMENT TRAPS

Sediment traps (1 m length and 10 cm diameter) were exposed in the deepest part of the lake close to the water sampling site at 15 and 28 m depth during 15 months (October 1989 to January 1991). The particulate material in the traps was collected approximately every three weeks and was subsequently freeze-dried until the analysis (Kuhn, 1992).

2.4. ANALYTICAL METHODS

2.4.1. Preconcentration Method for Zn

Zn was determined in filtered samples ($0.45\ \mu\text{m}$ pore size) by flame atomic absorption spectrometry after preconcentration. The preconcentration step involved the complexation of Zn with 8-hydroxyquinoline and the collection of the complexes on C-18 columns (Baker), in a procedure modified from Watanabe *et al.* (1981). Filtration and preconcentration were carried out under a clean bench with a laminar flow of filtered air. C-18 columns were cleaned before use by eluting them successively with 5 mL NTA ($5 \times 10^{-4}\ \text{M}$) solution, 5 mL 0.6 M HCl , 5 mL methanol, 5 mL 0.1 M HCl and 15 mL nanopure water (Nanopure, Barnstead). 8-hydroxyquinoline (HQ, p.a. Merck) was used without further purification. 200 mL of the filtered and acidified samples (measured by weight) were filled into polypropylene bottles, which had been cleaned by soaking in HNO_3 and nanopure water. To these 200 mL samples, 160 μL of a 8-hydroxyquinoline (HQ) solution were added to give a final concentration of $3.2 \times 10^{-5}\ \text{mol/L}$. The solution was then brought to $\text{pH}\ 9$ with 1.2 mL of NH_3 buffer solution (prepared from concentrated NH_3 and HCl (suprapure, Merck)), and immediately passed through a C-18 column fitted to a filtration apparatus. Zn retained on the column was eluted with $2 \times 5\ \text{mL}$ 0.6 M HCl ; the two elutions were measured separately, and the results were combined. The first elution usually contained over 90% of the recovered Zn. The preconcentration

factor was therefore 40 (for the 5 mL volume). Blank values of the whole procedure, including filtration, were usually $\leq 0.2 \mu\text{g/L}$ (3 nM). These values are (after preconcentration) close to the limit of determination by flame AAS ($10 \mu\text{g/L}$).

The recovery of the preconcentration procedure was checked by standard additions of Zn to lake water. Recovery of added Zn was in the range 90–100%. The recovery may be influenced by the presence of natural organic ligands for Zn and possibly of colloidal species. Acidification of the samples prior to the addition of HQ and subsequent buffering to pH 9 increases the recovery of Zn by releasing Zn from the natural complexes (Zweifel, 1992). Competition by other cations is not significant; only Mn(II) is sometimes present in the micromolar concentration range. Recovery of Zn was not influenced by the addition of Mn(II) in this range.

Reproducibility of the method was checked on eight parallel subsamples of lake water, which gave $1.65 \pm 0.07 \mu\text{g/L}$ on the original water, and after addition of $10 \mu\text{g/L}$ $10.7 \pm 0.2 \mu\text{g/L}$ (90% recovery in this case). The reproducibility of the sampling procedure was checked by taking three samples from the same depth and dividing each of them into two subsamples. The average of these six samples was $2.0 \pm 0.1 \mu\text{g/L}$.

Zn determination by this procedure was recently compared with direct measurements by ICP-MS; good agreement between the two methods was obtained.

2.4.2. Water and Sediment Analysis

Temperature, pH and oxygen were measured *in situ*, using a combined sensor (Züllig). Phosphate and silicate were determined by Auto-Analyzer spectrophotometric methods (Standard methods). Sulfide was determined using a H_2S specific electrode (Peiffer and Frevert, 1987). Suspended solids collected on cleaned $0.45 \mu\text{m}$ filters (from a volume of 0.5–1 L) and particulate material from the sediment traps were digested in aqua regia in a microwave digestion unit. Fe, Mn, Zn, Ca, Cr and Cu were determined by inductively coupled plasma emission spectrometry (ICP-AES), P by the molybdate spectrophotometric method (Standard methods). A sediment standard (NBS No. 1645) was used regularly in order to check the accuracy of the sediment digestion procedure. Total amount of suspended solids was determined by weight. The amount of suspended solids collected on filters was relatively small (about 0.5–3 mg/L); contamination problems were encountered in the digested samples from these filters. Particulate Zn data obtained in this manner were not reliable. Particulate Zn in the water column was therefore estimated from the concentrations of suspended particles and the Zn concentrations in the settling particles.

Figure 1. Depth profiles of dissolved ($< 0.45 \mu\text{m}$) Zn (nM, dots with solid lines, upper axis), temperature (dotted lines, lower axis), dissolved o-P (μM , dots with solid lines, upper axis) and Si (μM , squares with dotted lines, lower axis) in the water column of Lake Greifen from January 1990–January 1991.

3. Results

3.1. ZINC IN THE WATER COLUMN

The dissolved Zn concentrations in the lake water column are in the range 10–40 nM. The seasonal variations of dissolved Zn ($< 0.45 \mu\text{m}$), in comparison to the major nutrients phosphate and silicate (dissolved), over the year 1990 (Figure 1) indicate some common features, as well as some discrepancies between Zn and major nutrients. In January 1990, and again in December 1990 and January 1991, the lake is mixed, and the concentrations of Zn, phosphate and silicate are nearly homogeneous throughout the water column. During the summer stagnation period of the lake, the concentration variations of phosphate and silicate reflect the influence of algal productivity; dissolved phosphate is consumed to undetectable levels in the epilimnion, whereas silicate is still present. Although the results for Zn are not as systematic, Zn becomes depleted from the epilimnion (to 30–50% of the concentration during mixing) during summer stagnation. The mean concentration in the epilimnion decreases from about 30 nM in January to about 10–15 nM in July–August. The high values obtained in the April sampling are most probably due to contamination; these data were therefore not taken into account in the modeling.

High concentrations of phosphate and silicate in the hypolimnion are related to anoxic conditions (below about 10 m depth, from June to November), under which P and Si are released from the sediments and accumulate in the hypolimnion. Manganese (II) also accumulates in the anoxic hypolimnion (Johnson *et al.*, 1991), whereas no significant increase of the Fe(II) concentration was detected in the water column. Zn appears not to follow the same pattern as the nutrients and Mn(II) in the anoxic hypolimnion, and seems to be retained in the sediments under anoxic conditions. The Zn concentration decreases throughout the depth profile at the end of the stagnation period (November–December). Similar results on the concentrations of Zn in the water column were obtained during 1989. The data from the year 1990 will be discussed in more detail because sedimentation rates are available for this time.

Figure 2 illustrates the relationship between Zn and Si in the productive water layers (0–15 m) during summer stagnation in both years 1989 and 1990; the data from the anoxic part are excluded. Although a large scatter is observed, this figure indicates a relationship between the Zn and Si concentrations. The data from July and August, in 1989 and 1990, are close to each other. Correlation lines are drawn through the points from some of the sampling dates, in an attempt to derive stoichiometric ratios. Zn : Si ratios from the slopes of these lines are in the range $4\text{--}8 \times 10^{-4}$ (mol/mol), with an average value of 5×10^{-4} . Positive intercepts are obtained in all cases, indicating that Zn is still available when Si is used up. With suspended solid concentrations ranging from 1–4 mg/L in the epilimnion, and 0.5–1 mg/L in the hypolimnion, particulate Zn in the water column is calculated to about 1–7 nM, or 10–30% of total Zn.

Figure 2. Dissolved Zn in function of dissolved Si in the euphotic layers of Lake Greifen (0–15 m); each symbol represents a different sampling date in the time May 1989–September 1989 and March 1990–October 1990. Regression lines are drawn for some of the sampling dates: 26/7/89 ($\square$); 9/8/89 ($\blacktriangle$); 30/8/89 ($\bullet$); 11/7/90 ($\circ$); 8/8/90 (+); 19/9/90 ($\times$).

3.2. ZINC SEDIMENTATION

The composition of the particles collected in the sediment traps is given in detail by Sigg *et al.* (1995). The Zn concentrations in these particles range from 0.6–6.0 $\mu\text{mol/g}$ (average: 2.4 $\mu\text{mol/g}$). The average overall sedimentation rate is 3 $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ with a maximum of 7 $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ during summer. The average sedimentation rate of Zn, calculated from the overall sedimentation rate and the Zn content in the particles, is 0.34 $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (5.2 $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$), with a maximum of 0.54 $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (8.3 $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$). Differences between the two sediment traps at 15 and 28 m depth are small in most cases. Results are missing during March–April 1990 because one set of sediment traps could not be retrieved. The sedimentation rate of Zn exhibits seasonal variations (Figure 3), with one maximum during summer and another one during lake overturn (November–December). The maximum sedimentation rate of Zn during summer occurs at the same time as the depletion of Zn from the epilimnion. Various types of particles may be involved in the sedimentation of Zn (algae, calcium carbonate, manganese and iron oxides). In order to examine the role of these various particle types, the Zn sedimentation rates were calculated as a function of the sedimentation rate of

Figure 3. Sedimentation rates of Zn (identical data shown in **a**, **b**, thick lines) and concentrations of Zn in the settling particles (**c**) at 15 m (left) and 28 m lake depth. The graph further shows the evaluation of the types of particles involved in Zn sedimentation: The thin dotted lines (in **a**, **b**) represent calculated Zn sedimentation rates. **a**: Zn sedimentation calculated from sedimentation of algae (represented by particulate phosphate, PP) and manganese oxide, assuming a constant fraction of Zn in both particle types. **b**: Zn sedimentation calculated from sedimentation of calcite (represented by calcium) and manganese oxide. Further details are given in the text (Equations 1 and 2).

selected particles. For this analysis, it was assumed that two different particle types are involved in Zn sedimentation and that Zn is present in these particles at a constant fraction, neglecting variations of the Zn concentration in the water column and possible sorption/desorption kinetics. The first pair of particles tested was particulate phosphate (PP, representing algae) and particulate manganese (Mn). Using a least square fit procedure to minimize the difference of calculated and measured Zn flux, the following relation was found:

$$\begin{aligned}
 \text{Zn} \quad [\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}] \\
 &= 3.9 \cdot 10^{-2} \text{ PP} [\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}] \\
 &\quad + 6.1 \cdot 10^{-3} \text{ Mn} [\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}].
 \end{aligned}
 \tag{1}$$

Figure 4. Zn cycle in Lake Greifen: model used for the mass balance calculation. The figure depicts the elements of the model and the average Zn fluxes determined (normal font: values determined based on filed data; *italic*: values determined by mass balance calculation).

The Zn sedimentation calculated by Equation (1) corresponds surprisingly well to the observed Zn sedimentation (Figure 3a). The atomic Zn : P ratio characterized by Equation (1) is 0.018. Similar results were obtained when using calcite (represented by calcium) and manganese oxide as the two relevant particle types (Figure 3b):

$$\begin{aligned}
 \text{Zn} \quad [\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}] \\
 &= 2.2 \cdot 10^{-4} \text{ Ca} [\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}] \\
 &+ 1.1 \cdot 10^{-2} \text{ Mn} [\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}].
 \end{aligned} \tag{2}$$

Distribution coefficients between the particulate and the dissolved phases (K_D , L/kg) were calculated from the Zn concentrations in the filtered samples and in the settling particles (for the corresponding times and depths). K_D values range from 3×10^4 – 2.5×10^5 L/kg, with an average value of 1.1×10^5 L/kg.

3.3. MASS-BALANCE CALCULATION

The aim of the mass balance calculation was to combine the data on Zn concentrations in the lake, the data of the sediment traps and the information on the output of the lake. In this way, the processes governing the Zn cycle in lake Greifen were quantified on an integral scale.

The mass balance calculation (Figure 4) was performed for the period of 24 January, 1990 to 9 January, 1991. For the calculation, a water volume from the lake

surface down to 15 m, the depth level of the first sediment trap, was considered. This would correspond to $1.05 \times 10^8 \text{ m}^3$, or 70% of the lake volume. This water volume was considered as a completely mixed box. Water exchange with the deeper layers at 15 m depth had only a negligible effect on the distribution of Zn, and was thus neglected in the calculation. All terms in the mass balance equation but one could be directly determined by field data, as will be outlined below. The exception was the input of Zn to the lake, which was estimated by the mass balance. Previous calculations have shown that only a small fraction of Zn is present in the particulate form in the water column. Because data on particulate Zn are not reliable and because their incorporation into the mass balance calculations would only have a negligible effect, the more reliable concentrations of dissolved Zn were used as the total Zn concentration in the water column.

Equation (3) describes the mass balance:

$$\frac{\Delta M}{\Delta t} = J_{\text{in}} + J_{\text{atm}} - J_{\text{sed}} - J_{\text{out}} \quad (3)$$

with

$$\frac{\Delta M}{\Delta t} = \frac{M_{i+1} - M_i}{t_{i+1} - t_i}$$

being change in the total amount of dissolved Zn in the water volume (0–15 m) [$\text{kg} \cdot \text{d}^{-1}$] (Figure 5c), where M_i : total amount of Zn in the water volume V (0–15 m depth), for sampling date i (Figure 5b). Calculated from measured concentration profiles (Figure 1):

$$M_i = \sum_j C_{i,j} \cdot V_j, \quad (4)$$

where $C_{i,j}$: concentration of dissolved Zn measured on date i at depth j ($j = 0, 2.5, 5, 10$, and 15 m) [$\text{kg} \cdot \text{m}^{-3}$]; V_j : volume of water layer for which $C_{i,j}$ is representative [m^3].

t_i : day number for sampling date i [d].

J_{in} : input of Zn (Figure 5f). This value includes the input by the tributaries, and release from the sediment [$\text{kg} \cdot \text{d}^{-1}$]. J_{in} was estimated by the mass balance calculation. The concentration of Zn in the inflow, C_{in} was estimated in the following way, neglecting a possible release from the sediment:

$$C_{\text{in}} = \frac{J_{\text{in}}}{Q}, \quad (5)$$

where Q : flow rate of water (measured at water gauge at the lake outflow, assuming that inflow is equal to outflow, i.e. constant lake volume, Figure 5a) [$\text{m}^3 \cdot \text{d}^{-1}$].

J_{atm} : atmospheric deposition of Zn on the lake surface (measured value in Duebendorf) [$\text{kg} \cdot \text{d}^{-1}$] (Figure 5f); J_{sed} : Zn removed by sedimentation [$\text{kg} \cdot \text{d}^{-1}$] (Figure 5d). Measured by sediment traps.

Figure 5. Mass balance calculation for the Zn cycle in Lake Greifen, 1990. The grey bar indicates period II for which sediment trap data are missing. During this period, Zn sedimentation was calculated assuming an average Zn concentration in the inflow. Further details are given in the text.

J_{out} : elimination of Zn by the lake outflow [$\text{kg}\cdot\text{d}^{-1}$] (Figure 5e), calculated from:

$$J_{\text{out}} = Q \cdot C_{\text{epi}}, \quad (6)$$

where C_{epi} : concentration of dissolved Zn in the surface water (epilimnion, average of measured data at 0, 2.5, and 5 m lake depth) [$\text{kg}\cdot\text{m}^{-3}$].

The mass balance was calculated differently for two periods of time. From 24 January to 26 February, and 27 April to 1 January, 1991 (period I), the unknown input J_{in} (Figure 5f) and the corresponding input concentration C_{in} (Figure 5g) were calculated from the measured data. From 27 February to 26 April (period II) sediment trap data were missing. For this period, sedimentation was estimated using the average concentration in the inflow C_{in} estimated for period I. In the following, we will discuss the findings for the individual processes included in the mass balance calculation.

Total amount of Zn, M (Figures 5b and 5c): The total amount of dissolved Zn (M_i) in the water volume above 15 m varies within a factor of 2 between 103 and 213 kg. The highest values are observed at the beginning of the period (January 1990) and in May; lowest values are observed in March and in the period from June to September, during which a slight decreasing trend can be identified. During the end of the period (November/December), intermediate values are measured. The dynamics of the total amount of Zn in the lake reflect the interaction of the three processes discussed below.

Sedimentation J_{sed} (Figure 5d): The settling flux of Zn, J_{sed} , was calculated using the values measured in the sediment traps at 15 m extrapolated to the entire lake area (A), assuming that Zn is transported either to the lower water depths or to the sediment located between 0 and 15 m depths. The two maxima (observed from June to August, and in December) were discussed above. They may be attributed to the settling of algae or calcite (June to August), respectively, and to the settling of particulate manganese (December).

The estimated Zn sedimentation for period II, using an average concentration C_{in} of Zn in the inflow, indicates a sedimentation peak in March. This peak may be attributed to the first algae bloom in spring, reflected in the depletion of P and Si observed in March (see Figure 1). On the average (period I), sedimentation is responsible for about 87% of Zn elimination from the lake water column, which corresponds to an average elimination of $2.8 \text{ kg}\cdot\text{d}^{-1}$.

Zn outflow, J_{out} (Figure 5e): Zn in the outflow is only of minor importance for the elimination of Zn from the lake (average for period I: $0.4 \text{ kg}\cdot\text{d}^{-1}$, 13% of total elimination). The dynamics reflect the combined influence of water flow Q and epilimnetic Zn concentration, C_{epi} .

Zn input, J_{in} , from inflow and sediment release (Figures 5f and 5g): For period I, J_{in} was estimated by means of the mass balance. This input ranges from 0.1 to $5.0 \text{ kg}\cdot\text{d}^{-1}$, with an average of $2.2 \text{ kg}\cdot\text{d}^{-1}$. It corresponds to 74% of the total zinc input to the lake. The maximum values of up to $5.0 \text{ kg}\cdot\text{d}^{-1}$ in June and July seem to

be due to storm water input (Figure 5a), whereas the peak value in December may be due either to remobilization from the sediments, induced by oxygen reaching again the sediment/water-interface, or to an input by the inflow. The average inflow concentration of $6.9 \text{ mg} \cdot \text{m}^{-3}$ (105 nM) obtained for period I was used to determine the sedimentation rate of zinc during period II.

Atmospheric Zn input, J_{atm} (Figure 5f): Using the atmospheric deposition rate of $0.09 \text{ mg Zn} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ found in Duebendorf (about 10 km from Lake Greifen; Sigg and Zobrist, 1989), an input of $0.76 \text{ kg} \cdot \text{d}^{-1}$ to the lake is calculated. This value corresponds to 26% of the total Zn input to the lake.

The mass balance calculation presented is a first approach to model the Zn cycle in Lake Greifen. A more sophisticated, dynamic model could describe the temporal and spatial variation of Zn in Lake Greifen by means of differential equations which include all relevant transport and transformation processes (as done for manganese by Johnson *et al.*, 1991). Preliminary model calculations, conducted using CHEMSEE (Ulrich, 1996), have shown, however, that the data presently available do not allow the setup of such a model. Zn seems to sorb to at least two different particle types (Figure 3). Furthermore, sorption of Zn on particles cannot be described by a simple equilibrium partitioning model; in particular, uptake and binding by algae is not fully reversible upon sinking of algae. Hence, necessary prerequisites to set up a dynamic model would be:

- better identification of the particles relevant to the sorption of Zn;
- quantification of sorption/desorption or uptake/release kinetics of Zn to those particles;
- experimental quantification of the fluxes of those particles, including their short term variations in the order of days (Sturm *et al.*, 1982), which cannot be neglected in a model;
- a direct estimate of the input of zinc to the lake.

4. Discussion

Several facts indicate links between seasonal variations of Zn concentrations and the biological processes in this lake. The sedimentation rates, as given by Equations (1) and (2) can be related to the sedimentation of algae (represented by PP) and of manganese oxide. Although the sedimentation rates can also be related to calcium carbonate (Equation (2)), it seems likely that algae are more important, because of the low Zn concentration of particles with high calcium carbonate content (Figure 3c). The presence of calcium carbonate in the settling particles is actually a consequence of algal productivity. Investigations of the Zn speciation in Lake Greifen (Xue *et al.*, 1994, 1995) indicate that a relatively large fraction of Zn is present as aquo Zn^{2+} ions and as weak complexes and is thus easily available for interactions with the biota.

Correlations of Zn with nutrients in the water column may be expected if uptake and release by phytoplankton affect these elements in a similar manner, and

if other processes are not important. The relationships between Zn concentrations and nutrients in the water column of Lake Greifen are much less obvious than those observed in the oceans, as illustrated by Figures 1 and 2. Although Zn decreases in the epilimnion at the same time as the nutrients, only poor correlations between Zn and Si (or Zn and P) are observed; Zn to P correlations are difficult to observe, because P becomes completely depleted in the epilimnion during the stagnation period. A characteristic Zn : Si ratio may be expected in diatoms; Zn : Si ratios observed in the water column also depend, however, also on the relative abundance of diatoms and other algae, and may therefore vary within a certain range.

The relatively high Zn concentrations in the inputs and the excess of Zn over Si (and over P) indicate that Zn inputs exceed the requirements of algae for Zn as an essential trace element, and that Zn cannot be limiting in this system. Furthermore, few data are available within the productive layer, which is only few meters deep. Recycling processes within the productive layer, e.g. during periods with high zooplankton activity and consumption of the algae, may also influence the concentrations of Zn and major nutrients in different ways.

The ratios of Zn : Si derived here can be compared with those obtained in other systems, in order to examine whether characteristic ratios for algal material are observed. From the average molar Zn : Si ratio ($\approx 5 \times 10^{-4}$), estimated from the data in Figure 2, a Zn : P ratio $\approx 2.5\text{--}5 \times 10^{-3}$ is derived, using a Si : P ratio $\approx 5\text{--}10$, that is obtained from the corresponding profiles. This ratio is similar to that found in algae collected in this lake, as well as in some freshwater algae cultures (Kiefer, 1994). It is however lower than the estimate obtained from Equation (1) from the sedimentation rates, which represents an upper limit of this ratio (0.018). Higher ratios, namely Zn : P = 0.03–0.04, were obtained by Reynolds and Hamilton-Taylor (1992) in Windermere during a diatom bloom. Correlation between Zn and Si in depth profiles in Lake Sammamish gave a ratio Zn : Si = 5.6×10^{-5} (Balistrieri *et al.*, 1992). The dissolved Zn concentrations are, however, lower in this case (2–12 nM) than those reported here for Lake Greifen. The ratio of Zn : Si derived from oceanic profiles is Zn : Si = 5×10^{-5} (Bruland, 1980). Data on the composition of marine plankton indicate similar Zn : P ratios as calculated here (Zn : P $\approx 1\text{--}2 \times 10^{-3}$) (Bruland *et al.*, 1991). In marine algae, the Zn : C ratio in the cells is regulated within a certain range of free Zn^{2+} concentrations, whereas it increases at higher Zn^{2+} (Sunda and Huntsmann, 1992). In a similar way, the Zn intracellular content of the freshwater alga *Scenedesmus subspicatus* is regulated within a narrow range when Zn^{2+} varies from 10^{-14} to 10^{-9} M (Knauer *et al.*, 1995). At higher Zn^{2+} , the Zn contents of algae may also increase.

No correlations between Zn and nutrients are apparent in the anoxic hypolimnion of Lake Greifen. The concentration profiles of the nutrients may not be explained solely by the uptake by algae in the epilimnion, and mineralization and release in the deeper layers, because the release of nutrients from the sediments under anoxic conditions strongly influences their distribution in the water column. It is obvious, from the shape of the profiles, that there is no Zn release (or only very

small amounts) from the sediments under anoxic conditions. Zn associated with manganese oxides in the particulate phase is not released together with manganese during anoxia. Zn must thus be retained in the sediments by binding to other particles. Although the Zn concentrations in the water column do not exceed the solubility product of $\text{ZnS}_{(s)}$, binding to sulfidic particles, e.g. to FeS formed in the sediments (Morse and Arakaki, 1993) may be a possible mechanism. This behavior is in agreement with other studies of Zn in lakes with anoxic conditions (Morfett *et al.*, 1988; Balistrieri *et al.*, 1992; Hamilton-Taylor and Davison, 1995).

The mass balance calculations reveal the major characteristics of the Zn cycle in lake Greifen. Total Zn input into the lake seems to vary from 0.9 to 5.8 $\text{kg}\cdot\text{d}^{-1}$ (average 2.2 $\text{kg}\cdot\text{d}^{-1}$). Of this, 26% may be assigned to atmospheric input, 74% to the inflows (including probably a rather minor release from the sediments at the end of the stagnation period, under oxic conditions). Neglecting the sediment release, an average inflow concentration of Zn of 105 nM is estimated, which corresponds to average values found at three comparable sampling stations on rivers in densely populated areas (92, 168, 199 nM; Hydrologisches Jahrbuch, 1990). The predominant part of Zn is, partly after uptake by algae, incorporated in the lake sediments (87%), only 13% is eliminated by the lake outflow. Internal recycling of Zn seems to play a minor role only. More precise information on Zn concentrations in the inflow would be necessary, however, to verify these findings.

The seasonal variations of Zn in the water column of Lake Greifen confirm the idea that biological mechanisms of uptake and binding are significant for the removal of Zn to the sediments. These findings are in agreement with observations in other lakes (Windermere (Reynolds and Hamilton-Taylor, 1992); Sammamish (Balistrieri *et al.*, 1992); and Baldegg (Baccini and Joller, 1981)).

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