Zinc isotope composition of settling particles as a proxy for biogeochemical processes in lakes: Insights from the eutrophic Lake Greifen, Switzerland

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Abstract

The isotope composition of zinc (Zn) was determined in settling particles collected monthly over a year in the hypolimnion of the eutrophic Lake Greifen (Switzerland) in order to explore the potential of this novel isotope system as a proxy for biogeochemical processes in aqueous environments. Significant variation in $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ of 0.9‰ (where $\delta^{66}\text{Zn}_{\text{JMC3-0749L}} = [\{^{66}\text{Zn} : ^{64}\text{Zn}\}_{\text{sample}} / \{^{66}\text{Zn} : ^{64}\text{Zn}\}_{\text{JMC3-0749L}} - 1] \times 1000$) was found throughout the seasonal cycle of productivity. The most negative $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ values (down to $-0.66\text{‰} \pm 0.08\text{‰}$) were observed during the productive summer period from June to September, when the Zn in the settling particles was predominantly associated with organic material, and when Zn concentrations in the epilimnion were lowest. This observation is likely explained with preferential uptake of the light Zn isotopes during algal growth. During the other months, the Zn in the sediment traps showed higher $\delta^{66}\text{Zn}$ values, reflecting increasing contributions of anthropogenic or lithogenic components. The average isotopic signature of the settling particles during the autumn–winter–spring period ($\sim -0.2\text{‰}$ for $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$) was somewhat lower than typical for anthropogenic and natural sources, and this possibly reflects the effect of the preferential adsorption of lighter dissolved Zn isotopes onto the settling particles. We suggest that Rayleigh fractionation plays a minor role in controlling the isotopic composition of the settling particles in the lake. Our work demonstrates the presence of an obvious seasonal cycle in $\delta^{66}\text{Zn}$, and this suggests that Zn isotopes can be employed to study nutrient utilization and other biogeochemical processes in lakes and other aquatic environments.

Zinc (Zn) is an essential cofactor of many proteins and enzymes, for example, in carbonic anhydrase, which mediates the conversion of CO_2 to HCO_3^- in the photosynthetic process (Frausto Da Silva and Williams 2000). Consequently, Zn is an essential micronutrient for planktonic algae, and it plays an important part in the biogeochemical cycle of various elements in aquatic systems. In oceans and lakes alike, Zn shows a nutrient-like vertical concentration profile similar to silica and nitrogen: it is depleted in the surface waters resulting from uptake by algae (Bruland 1980; Reynolds and Hamilton-Taylor 1992). It has been proposed that the Zn stable isotope system may develop into a tracer for nutrient availability in both modern and ancient waters (Albarède 2004; Anbar and Rouxel 2007). Preliminary analyses of Zn isotopes in seawater and algae agree with the assumption that biological activity in the surface waters preferentially consumes the light isotope, leaving the remaining dissolved Zn pool isotopically heavy (Bermin et al. 2006; John et al. 2007a). The link between Zn isotopes and productivity was first explored by Maréchal and coworkers (Maréchal et al. 2000) for the oceans. They inferred that depletion of light Zn isotopes in ferromanganese nodules was due to biological activity in the upper water column, though this interpretation is challenged by the fact that Zn is regenerated in the deep ocean. Nevertheless, sediment trap samples from the same study revealed a seasonal isotopic fluctuation consistent with biological pumping during the high-productivity period in a coastal upwelling region. A

subsequently established Zn isotope record in the carbonate fraction of sediment cores from the equatorial Pacific showed significant variations, which were interpreted as a function of strength of upwelling, nutrient availability, and hence productivity (Pichat et al. 2003). Preliminary results for settling particles from a Swiss lake showed variation of Zn isotopes over a few months related to the spring algal bloom and subsequent depletion of Zn in surface waters (Cloquet et al. 2007).

Unlike most other transition metals, Zn has only one common oxidation state, so whereas for elements such as iron (Fe) and copper (Cu), redox reactions can be a source of large fractionation, uptake by plankton may be among the most prominent processes affecting Zn isotopes in the environment. The range of reported $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ (where $\delta^{66}\text{Zn}$ is expressed relative to the Johnson–Matthew Company batch 3-0749L standard) for biological materials extends from -0.9‰ to $+0.8\text{‰}$; this range contrasts with igneous rocks (basalts, granites, granodiorites, and andesites) or “common” anthropogenic sources, which tend to fall within the range of $+0.1\text{‰}$ to $+0.6\text{‰}$ (Wilkinson et al. 2005; John et al. 2007b; Sonke et al. 2008; Sivry et al. 2008).

The Zn isotope signatures observed in settling particles may be affected, however, by other biogeochemical processes, such as adsorption of dissolved Zn onto cell walls and mineral surfaces. Systematic enrichment of heavy Zn isotopes ranging between $+0.19\text{‰}$ and $+0.43\text{‰}$ has been shown in cultured diatoms cells depending on species and experimental conditions such as pH, ion strength, and speciation (Gélabert et al. 2006). John and coworkers (John et al. 2007a) determined fractionation factors between

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Fig. 1. (A) Sedimentation rate of Zn expressed in $\text{mg m}^{-2} \text{d}^{-1}$; (B) Zn isotope composition expressed in $\delta^{66}\text{Zn}$ relative to the JMC3 0749L Zn standard (error bars are $\pm 2\sigma$ for a minimum of three replicate analyses); and (C-E) sedimentation rates of Fe, C_{org} , and Mn in settling particles collected in traps at 15 m and 28 m depth between November 1989 and January 1991 expressed in $\text{mg m}^{-2} \text{d}^{-1}$. Samples are missing during March-April 1990 because one set of sediment traps could not be retrieved.

water and algae cell ranging from -0.05‰ to $+0.38\text{‰}$ for unwashed cells and up to 0.8‰ for washed cells (depending on the $[\text{Zn}]$ in solution). Similarly, in stream waters affected by historical mining, Borrok and coworkers (Borrok et al. 2008) observed an apparent isotopic separation process between dissolved and solid Zn of $\sim 0.3\text{‰}$ for $^{66}\text{Zn}:^{64}\text{Zn}$.

The aim of the present work was to explore the potential of the Zn isotope system to characterize biogeochemical processes in the aqueous environment. This was achieved by analyzing settling particles collected in the hypolimnion of Lake Greifen in Switzerland over a year with respect to the seasonal cycle of productivity and nutrient availability.

Site description and previous work

Lake Greifen is a eutrophic lake located in a densely populated area, 12 km east of Zürich, Switzerland. The surface area is $8.5 \times 10^6 \text{ m}^2$, its volume is $150 \times 10^6 \text{ m}^3$, and the maximum depth is 32 m. The alkalinity is ~ 3.6 4.1 mmol L^{-1} , and the pH ranges between 7.5 and 8.5, with variations in time and depth. Dissolved organic carbon is $3\text{--}4 \text{ mg L}^{-1}$ in the water column (Xue et al. 1995). The estimated residence time of the water is 1.1 yr (Sigg et al. 1996), and the estimated residence time of Zn is $120 \pm 30 \text{ d}$ (Santschi 1984). The tributaries of the lake are loaded with nutrients and pollutants from sewage and agriculture. The predominant part of Zn (87%) is incorporated in the lake sediments after uptake by algae, and only 13% is eliminated by the lake outflow. Internal recycling of Zn from sediments plays a minor role (Sigg et al. 1996). Seasonal cycles of productivity and thermal stratification lead to variable physiochemical conditions, which control the cycling of trace elements in the lake system. Thermal stratification lasts approximately from May to December, and lake overturn usually takes place in December to January. During summer stagnation, from approximately June to December, the hypolimnion becomes anoxic below 10-m depth. These changes in redox state mean that there is an active manganese (Mn) cycle taking place. Manganese oxides form a large part of the settling particles during overturn, and a peak in their sedimentation rate coincides with that of Zn, indicating that adsorption to Mn oxides is a mechanism of Zn sedimentation (Sigg et al. 1995). The composition of settling particles caught in sediment traps reflects the seasonal variations in productivity and redox cycles. The sedimentation rate of organic carbon (C_{org}) increases in the summer months (June to August) due to the increase in productivity. The maximum sedimentation rate of Zn during summer occurs at the same time. The $[\text{Zn}]$ profile in the water column throughout the seasonal cycle is similar to major nutrients such as P and Si. Zinc is depleted from the epilimnion during summer stagnation to between 30% and 50% of its concentration during mixing, but is never completely depleted (Sigg et al. 1995). During lake overturn, $[\text{Zn}]$ is homogeneous throughout the water column. Investigations of the Zn speciation (Xue and Sigg 1994; Xue et al. 1995) indicate that between 5% and 10% of total dissolved Zn is present as aqua Zn^{2+} ions and 30% to

40% is present as weak complexes and is easily available for interaction with the biota. The spatial and temporal evolution of the $[\text{Zn}]$ depth profile at the Lake Greifen is shown and discussed in all detail elsewhere (Sigg et al. 1995, 1996).

Methods

Sample description and elemental analysis The settling particles were collected and their elemental concentrations determined during a previous study (Sigg et al. 1995, 1996). We only give a short summary here. Sediment traps were employed in the deepest part of the lake at depths of 15 m and 28 m and retrieved every 3 weeks for 15 months from October 1989 to January 1991. Samples are missing during March–April 1990 because one set of sediment traps could not be retrieved. The sedimentation rates were quantified by weighing the dry material. Samples were freeze-dried and stored as dry powders in the dark at 4°C at Eawag (Switzerland) until further analysis. The settling particles were digested with HCl-HNO_3 using microwave digestion. Iron, Mn, Zn, and Ca were determined by inductively coupled plasma optical emission spectrometry (ICP-OES), P was determined by the molybdate spectrophotometric method, and organic C and N were determined by CHN analyzer.

Zinc isotope analysis For the isotope analysis, samples were shipped to Imperial College London (IMP, U.K.) in February 2007. Approximately 0.1 g of each settling particle sample was digested in 5:2:1 mL of Aristar-grade (VWR) concentrated $\text{HF-HNO}_3\text{-HClO}_4$ acid mixture in open Teflon vessels in a heating block at 90°C for 3 h, 140°C for 3 h, and 190°C for 10 h (Thompson and Walsh 1989). Evaporated fractions were taken up in 6 mL of 7 mol L^{-1} HCl and heated for 24 h at 80°C before being evaporated. Finally, the samples were taken up in 2 mL of ultrapure grade (Romil) 7 mol L^{-1} HCl.

Ion-exchange chromatography was used to separate Zn fractions from matrix components prior to isotope analysis (Chapman et al. 2006). Recoveries were monitored and yielded $>95\%$. All isotopic measurements were made using the IsoProbe multicollector ICP mass spectrometer (Thermo Scientific) connected to an Aridus desolvating nebulizer (Cetac Technologies). Instrumental background and acid matrix blank corrections were performed using on-peak blank measurements taken before every sample and standard. Sample and standard measurements were made by taking 25 five-second integrations. All samples were spiked with a Cu standard to act as an internal mass discrimination monitor. Standards were made up using in-house Cu and Zn solutions (IMP Zn and IMP Cu). Sample and standard solutions for each analytical run were concentration matched to within $\pm 10\%$. Mass discrimination effects were corrected using a combined sample-standard bracketing and interelement correction procedure. Nickel (Ni) interferences on ^{64}Zn were carefully monitored. Full descriptions of the analytical protocol and the in-house solutions are given elsewhere (Mason et al. 2004; Peel et al. 2007; Weiss et al. 2007).

The value of $\delta^{66}\text{Zn}$ was calculated using $\delta^{66}\text{Zn} = ([R_{\text{sample}}]:[R_{\text{standard}}] - 1) \times 1000 (\text{‰})$, where R_{sample} is

Table 1. Zn isotope composition expressed as $\delta^{66}\text{Zn}$ relative to the JMC3 0749L standard, $\pm 2\sigma$ determined from a minimum of three replicate analyses, total sedimentation rates for settling particles, and sedimentation rates of Zn, C_{org} , P, N, Ca, Fe, and Mn (taken from Sigg et al. 1995) at 15 m and 28 m depth.

Sampling depth	Sampling period		$\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ (‰)	$\pm 2\sigma$	Total ($\text{g m}^{-2} \text{d}^{-1}$)	Zn ($\text{mg m}^{-2} \text{d}^{-1}$)
	Start	End				
15 m	18 Oct 89	22 Nov 89	0.11	0.08	1.64	0.25
	22 Nov 89	13 Dec 89	0.16	0.23	2.17	0.48
	13 Dec 89	16 Jan 90	0.24	0.04	1.18	0.37
	16 Jan 90	27 Feb 90	0.44	0.08	1.56	0.36
	27 Apr 90	22 May 90	0.08	0.05	1.58	0.17
	22 May 90	13 Jun 90	0.22	0.12	6.83	0.48
	13 Jun 90	13 Jul 90	0.63	0.08	7.73	0.54
	13 Jul 90	03 Aug 90	0.18	0.04	7.34	0.44
	03 Aug 90	31 Aug 90	0.33	0.03	3.22	0.16
	31 Aug 90	28 Sep 90	0.31	0.05	2.48	0.15
	28 Sep 90	23 Oct 90	0.01	0.03	1.50	0.16
	23 Oct 90	09 Nov 90			1.99	0.20
	09 Nov 90	28 Nov 90			2.38	0.36
	28 Nov 90	19 Dec 90	0.22	0.15	1.88	0.64
	19 Dec 90	10 Jan 91	0.09	0.07	1.07	0.35
28 m	18 Oct 89	22 Nov 89	0.21	0.11	1.46	0.22
	22 Nov 89	13 Dec 89	0.34	0.05	1.70	0.29
	13 Dec 89	16 Jan 90	0.37	0.05	1.37	0.42
	16 Jan 90	27 Feb 90	0.18	0.16	2.12	0.34
	27 Apr 90	22 May 90	0.04	0.14	2.50	0.48
	22 May 90	13 Jun 90	0.23	0.06	6.69	0.60
	13 Jun 90	13 Jul 90	0.54	0.06	7.07	0.49
	13 Jul 90	03 Aug 90	0.37	0.14	6.12	0.37
	03 Aug 90	31 Aug 90	0.66	0.08	2.84	0.11
	31 Aug 90	28 Sep 90	0.60	0.10	2.11	0.25
	28 Sep 90	23 Oct 90	0.21	0.10	1.50	0.15
	23 Oct 90	09 Nov 90	0.44	0.06	1.65	0.17
	09 Nov 90	28 Nov 90	0.17	0.13	2.04	0.29
	28 Nov 90	19 Dec 90			1.46	0.41
	19 Dec 90	10 Jan 91	0.19	0.10	1.33	0.52

the $^{66}\text{Zn}:^{64}\text{Zn}$ ratio of the sample, and R_{standard} is the $^{66}\text{Zn}:^{64}\text{Zn}$ ratio of the bracketing IMP Zn standard. All $\delta^{66}\text{Zn}$ results are reported relative to JMC 3-0749L Zn, which has a $\delta^{66}\text{Zn}$ value relative to the IMP Zn solution of $0.09\text{‰} \pm 0.05\text{‰}$ (± 2 SD, $n = 12$). Reproducibility was assessed by repeated measurement of the BCR 280 standard (lake sediment) and was $\pm 0.08\text{‰}$ (± 2 SD, $n = 12$). Errors on the reported $\delta^{66}\text{Zn}$ values are two standard deviations calculated from a minimum of three replicate analyses. Precision for a single-element Zn solution (Romil) over a period of 3 yr was better than $\pm 0.04\text{‰}$. Internal precision for each measurement was better than 0.002‰ (2 SE at 95% confidence level) for all ratios. Procedural blank contributions were typically 20 ng of Zn, which was $<3\%$ and insignificant. Accuracy was checked using repeated analyses of the international geological standard BCR 1, and the $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ values agreed within error (0.33 ± 0.07) with previously published values (Cloquet et al. 2007).

Results

The Zn isotope ratios (expressed using $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ in ‰) of the settling particles and the sedimentation rates of

Zn, C_{org} , Mn, and Fe (expressed using fluxes in $\text{mg m}^{-2} \text{d}^{-1}$) at both depths over the year are shown in Fig. 1 and Table 1. The value of $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ varies by 0.9‰, ranging from -0.66‰ to $+0.21\text{‰}$. This falls largely within the previously determined isotopic range of Zn in terrestrial geological material of -0.4‰ to $+1.4\text{‰}$ (Cloquet et al. 2006). Samples collected during the summer are below this range ($\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ between -0.44‰ and -0.66‰) yet above the lowest measured $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ value of

-0.91‰ reported for palm leaves (Viers et al. 2007). The δ values and seasonal pattern for both the 15-m and 28-m sediment traps are similar, as may be expected from their similar chemical and mineralogical composition. The $\delta^{66}\text{Zn}$ fluctuates throughout the year, but peaks of isotopically heavy Zn are seen in May and October, and the isotopically lightest values occur between June and September. During the autumn, winter, and early to midspring months (November to April), when biological activity is small (in general lower C_{org} fluxes), the average value of $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ is $\sim 0.2\text{‰}$ at both depths; this is significantly higher than during the summer months (June to September), which average $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ values of -0.36‰ and -0.54‰ at 15 m and 28 m, respectively, and the late summer (October), which showed $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$

Table 1. Extended.

C _{org} (mg m ⁻² d ⁻¹)	P (mg m ⁻² d ⁻¹)	N (mg m ⁻² d ⁻¹)	Ca (mg m ⁻² d ⁻¹)	Fe (mg m ⁻² d ⁻¹)	Mn (mg m ⁻² d ⁻¹)
180	6.6	25.5	288	9.2	1.2
348	13.8	58.7	237	18.2	24.3
118	4.9	17.0	181	11.9	43.9
101	3.6	13.1	266	21.8	6.9
183	5.2	32.5	190	7.1	1.5
279	8.0	38.3	2253	7.6	2.3
413	11.7	52.0	2395	17.3	2.1
370	9.1	55.5	2362	8.2	0.8
277	7.3	39.2	903	7.2	0.7
202	5.1	28.5	641	6.9	0.7
186	3.7	24.0	265	9.2	0.4
164	4.9	25.9	369	16.7	2.7
229	7.0	37.7	418	21.3	7.6
188	6.4	32.1	305	18.9	42.9
87	3.8	13.8	180	8.4	32.5
137	4.7	21.1	294	10.6	1.6
253	10.1	43.3	204	17.1	19.3
143	5.6	20.0	210	14.5	50.0
137	5.1	17.2	361	33.2	14.2
275	11.2	63.4	225	15.4	22.0
301	10.8	39.4	2158	14.9	18.7
351	10.9	47.5	2239	15.8	6.2
309	7.8	48.0	1975	6.8	1.3
223	7.3	33.4	812	6.3	1.1
191	4.2	27.5	578	9.4	0.7
188	3.9	25.4	260	13.4	0.6
181	5.3	25.9	291	14.7	1.6
183	5.5	26.9	388	22.8	3.5
133	6.0	20.5	252	17.9	17.5
105	4.7	17.3	223	11.9	50.6

values of +0.21‰ and +0.01‰ at 28 m and 15 m, respectively. Low $\delta^{66}\text{Zn}$ values coincide in general with increased C_{org}, P, and total sedimentation rates in the summer months, and high δ values in May and October show a possible link to a decrease in these rates (Table 1).

Discussion

Autumn winter spring period The average isotope signature during the autumn-winter-spring period is around 0.2‰ for $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ at both sampling depths. This is lower than expected if the Zn were derived from natural soil dust only, which ranges approximately between +0.2 to +0.6 (Albarède 2004; Wilkinson et al. 2005; Cloquet et al. 2006). However, the lake is situated in an area of urban and agricultural land, and the dominant sources of Zn via rivers and via atmospheric deposition are of anthropogenic origin (Sigg et al. 1995, 1996). Previous work has established that over the period of a year, the input of Zn to the lake consists of ~74% from tributaries and ~26% from atmospheric deposition. The main sources of Zn in the tributaries are from house installations and Zn contained in manure, while atmospheric deposition is mainly derived from waste incineration (Sigg et al. 1995, 1996).

Sonke et al. (2008) suggested that the global pool of anthropogenic Zn emissions, including waste combustion, mining dust, automotive fuel, and brake emissions, clusters around $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ values of +0.1‰ to +0.2‰. As such, anthropogenic Zn is likely less enriched in the heavy isotope than natural sources. More depleted Zn isotope signatures were determined in rainfall in Montpellier, France, ranging between 0.1‰ and 0.2‰ (Cloquet et al. 2007), and in aerosols collected in Sao Paulo, Brazil and around a smelter in Belgium, ranging between -1.0‰ and +0.5‰ (Gioia et al. 2008). Zinc isotope studies of polluted rivers have been conducted in the Seine, France (Chen et al. 2008), and in catchments in the Iberian Pyrite Belt (Spain), in Montana (U.S.), and in Colorado (U.S.) (Borrok et al. 2008). The study in the Seine River Basin reported $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ values of 0.02‰ to 0.07‰ for roof runoff in the Paris area, with a slightly lower $\delta^{66}\text{Zn}$ value of 0.10‰ for leached roof cover (Chen et al. 2008). A higher value of +0.28‰ was found for untreated sewage and water entering a wastewater treatment plant, although the total output of Zn from the plant (dissolved and suspended) was lower, showing a $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ value of +0.07‰. In agricultural areas, Zn entering the Seine River was isotopically heavier, showing values such as +0.19‰ to

+0.42‰ for N, P, and K fertilizers, and +0.31‰ for treatment sludge reused as compost typifying the inputs (Chen et al. 2008). The average $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ value for stream waters draining abandoned historical mining districts in Spain and the U.S. varied from +0.02‰ to +0.46‰ (Borrok et al. 2008). In conclusion, the Zn (dissolved and solid) delivered to Lake Greifen via the atmosphere and the tributaries is likely to be heavier than the measured value of -0.2‰ in the settling particles. (Atmospheric deposition and river waters were not collected during the sampling period.) However, Borrok et al. (2008) determined an apparent separation factor of 0.3‰ for $\delta^{66}\text{Zn}$ between the dissolved and the solid Zn reservoir, with the particles taking up the lighter Zn isotope. Such an isotopic offset applied to the measured value of -0.2‰ in the settling particles leaves the dissolved Zn with a $\delta^{66}\text{Zn}$ value of around +0.1‰. This calculated $\delta^{66}\text{Zn}$ value then falls within the previously postulated “common anthropogenic Zn” value by Sonke et al. (2008) and John et al. (2007b).

A potential process that can explain the offset between dissolved Zn and sinking particles is the adsorption of isotopically light Zn on mineral particles (Pokrovsky et al. 2005; Balistrieri et al. 2008; Juillot et al., 2008). Batch experiments with Zn and various oxides showed that the separation factor between solution and solid (where $\Delta^{66}\text{Zn}_{\text{solution-solid}} = \delta^{66}\text{Zn}_{\text{solution}} - \delta^{66}\text{Zn}_{\text{solid}}$) ranges between -0.6‰ and +0.2‰, depending on speciation and solution pH. For birnessite ($\delta\text{-MnO}_x \cdot n\text{H}_2\text{O}$), a $\Delta^{66}\text{Zn}_{\text{solution-solid}}$ value of $0.17\text{‰} \pm 0.06\text{‰}$ was determined. This fractionation could partly account for the observed lighter Zn in the settling particles in this study. The Mn phases in Lake Greifen have not been determined, but in other Swiss lakes with comparable water chemistry, the principle Mn-oxide in sediments is vernadite, a structure similar to $\gamma\text{-MnO}_2$ and somewhat different from birnessite (Wehrli et al. 1995). Another factor that contributes to the lighter than expected Zn isotope signature in the settling particles during the autumn/winter/fall period is a possibly significant contribution from algae (see, e.g., the significant C_{org} flux during the early autumn).

Summer high-productivity period The settling particles display the most negative $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ values (up to -0.66‰) during the summer high-productivity period (June to September). During this period, organic matter and calcite with very little Mn dominate the composition of the particles, and these samples are representative of algal material (Table 1; Sigg et al., 1996). Organic carbon (C_{org}) is well correlated with P and N, indicating that biological material is the common source. The molar Zn:P ratios in summer samples appear close to that expected of algae (0.01–0.03), implying that a significant fraction of the sedimenting Zn is associated with organic material, either incorporated in the cells or bound to the surface. Zinc in Lake Greifen is not released from the particles back to the water column by bacterial respiration, as evidenced by the high percentage of Zn removed from the lake system by sedimentation, and the lack of increase in [Zn] with depth in the hypolimnion (Sigg et al. 1996). This means that the isotopic composition of the

particles is unlikely to have changed significantly from that of the algae in the surface layers.

Recent experimental work on isotopic fractionation during Zn uptake by marine diatom cells under nonlimiting conditions (as is typical for Lake Greifen even during the summer high productivity) reported $\Delta^{66}\text{Zn}_{\text{cell-media}}$ (where $\Delta^{66}\text{Zn}_{\text{cell-media}} = \delta^{66}\text{Zn}_{\text{cell}} - \delta^{66}\text{Zn}_{\text{media}}$) of 0.8‰ (John et al. 2007a). This fractionation factor is representative for a low-affinity Zn transport pathway. The low $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ values of the settling particles in the summer are in line with algae taking up the light isotope preferentially. This suggests that externally adsorbed Zn is not making a major contribution to the $\delta^{66}\text{Zn}$ during the summer. Low contribution of adsorption on the freshwater algae is confirmed by culture experiments carried out under conditions relevant for Lake Greifen, in which total Zn concentration measured for algae was almost identical to intracellular Zn (Knauer et al. 1997).

Operation of a non-Rayleigh type fractionation mechanism? The $\delta^{66}\text{Zn}$ of settling particles increases markedly during the October collection period, up to the highest $\delta^{66}\text{Zn}_{\text{JMC3-0749L}}$ value of the year at 28-m depth ($0.21\text{‰} \pm 0.1\text{‰}$). The P and C_{org} sedimentation rates are at a low point at that time, indicating that the high-productivity summer period is at an end (Table 1; Fig. 1)

This heavy isotope signature of Zn could represent a Rayleigh effect where the high productivity of the summer bloom causes a depletion of Zn in the surface waters, and as the light isotope is removed preferentially, the remaining dissolved Zn pool becomes isotopically heavy. A similar explanation was suggested for observed Zn isotope patterns in settling particles at another Swiss lake (Cloquet et al. 2007), where the lowest isotope ratios occurred during the spring algal bloom, followed by a sharp increase when Zn became depleted in the water. We argue, however, against such a mechanism operating in Lake Greifen for the following reasons.

First, we note that the Zn concentrations in water, although lower than during the winter period, are still higher in the October samples compared to the summer samples (Fig. 2). Second, a plot of the measured isotope data and the fraction of dissolved Zn remaining in the lake water along with models for a Rayleigh-type and an equilibrium-type fractionation process (Fig. 3) (using the experimentally determined $\Delta^{66}\text{Zn}_{\text{cell-media}}$ of 0.8‰ and an initial δ value for dissolved Zn in the epilimnion of 0.1‰) does not support the operation of a Rayleigh-type fractionation mechanism. Third, we note that the increase of [Zn] during September and October in the lake appears to correspond to an increased water inflow (see fig. 5 in Sigg et al., 1996). This increase may be due to rain events, which may have brought more Zn into the lake, possibly bound to allochthonous particles. The composition of the particles (Table 1) indicates that the particles in the period between 28 September 1990 and 23 October 1990 contain more Fe than during summer, which could be indicative of allochthonous particles. So an alternative explanation would be that in October, more Zn is carried to the lake with allochthonous particles, where $\delta^{66}\text{Zn}$ is expected to be higher.

Fig. 2. Average concentration of dissolved Zn (in $\mu\text{g L}^{-1}$, samples passed through $0.45 \mu\text{m}$ filters) collected at various depths in the epilimnion (0 to 10 m) and hypolimnion (15 to 31 m) between January 1990 and January 1991. Data taken from Sigg et al. (1996).

In conclusion, our data suggest that seasonal variations in biological uptake, variations in input sources, and adsorption on mineral particles alike influence the Zn isotope composition of settling particles. This opens up the use of this new isotope system as a tracer of

biogeochemical processes in lakes. Figure 4 represents a preliminary attempt to summarize the most important processes leading to isotopic variability in a lake. Further work is warranted to confirm this model in lakes.

Fig. 3. Rayleigh (solid lines) and equilibrium fractionation (dotted lines) models (see Hoefs [2004] for relevant equations) for the uptake of dissolved Zn by algae in the epilimnion. The initial $\delta^{66}\text{Zn}$ value is $+0.1\text{‰}$, and the isotopic fractionation factor between algae and solution is 0.8‰ (see text for detailed explanations). Also plotted are the measured $\delta^{66}\text{Zn}$ values in the settling particles at 28 m depth vs. the Zn remaining in the epilimnion using the data given in Fig. 2 and normalizing against the highest $[\text{Zn}]$ measured on 25 January 1990 ($2.20 \mu\text{g L}^{-1}$).

Fig. 4. A preliminary isotope fractionation model for Zn during its biogeochemical cycle in a lake, showing the cycles during summer (top) and autumn winter spring (bottom). Assuming a separation factor of +0.3‰ between dissolved and particulate Zn (Borrok et al. 2008), we calculate a $\delta^{66}\text{Zn}$ signature of +0.1‰ for the dissolved Zn fraction. This value agrees well with the proposed “common anthropogenic Zn signature” (John et al. 2007b; Sonke et al. 2008). The offset between dissolved and sinking particles during the autumn winter spring period is possibly due to the adsorption of dissolved Zn onto mineral particulates such as manganese, aluminum, or iron oxides (Balistrieri et al. 2008; Juillot et al. 2008). In the summer, algae dominate the composition of the settling particulates. Algae preferentially take up the light ^{64}Zn isotope with a fractionation factor of -0.8‰ (John et al. 2007a), leading to the $\delta^{66}\text{Zn}$ signature of around -0.7‰ in the settling particles. Adsorption on the algae rich particles seems less important (Knauer et al. 1997). The calculated isotopic signature of dissolved Zn is in line with the range of previously determined atmospheric and riverine isotopic signatures (see text for references) and lies well on a mixing line between these two end members and their previously determined contributions (26% from the atmosphere and 74% from the rivers) to the lake (Sigg et al. 1995, 1996). The estimated values for atmospheric and riverine input are a best guess from the range of isotopic values measured in these sources. There is not a binary switch between sedimentation of mineral particles in the winter and algae in the summer; thus, there is a big arrow to the algae in the summer and a small arrow to the mineral and the reverse in the winter (big arrow to particles and a small arrow to algae).

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