

# Is phosphorus retention in autochthonous lake sediments controlled by oxygen or phosphorus?

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## Abstract

Eutrophication of various lakes on the Swiss Plateau was targeted in the 1980s by reducing external nutrient loading and installing aeration/oxygenation systems. For five eutrophic lakes, three of which have been artificially oxygenated and aerated for almost 20 yr, phosphorus (P) balances were established using input, water-column inventory, export via the outlet, and sediment core data. To separate the effects of aeration/oxygenation from the effects of P-input reduction, two measures of P retention were determined—the ratio of net sedimentation to input and the ratio of net sedimentation to gross sedimentation. A comparison among the five lakes shows that, presently, P retention does not differ significantly between lakes with aeration/oxygenation and lakes with an anoxic hypolimnion, whereas retention at times of maximum P concentrations in the 1970s and 1980s was significantly lower compared with retention in today's moderately eutrophic lakes. This is in agreement with the finding that net sedimentation in all lakes remained relatively constant between 280 and 950 kg km<sup>-2</sup>, independent of their P concentration. It is shown that constant net sedimentation is likely to prevail as long as P concentrations remain above a critical value of around 40 mg m<sup>-3</sup>. Constant net sedimentation indicates that permanent deposition of P is limited by the sediment's binding capacity. Oxidic conditions in the hypolimnion do not necessarily increase this capacity because redox-dependent P species may still be released within the anoxic bulk sediment and diffuse back into the water column. To characterize the P retention capacity of anoxic sediments, we suggest that the P burial rate be determined from dated sediment cores rather than from input/output balances.

In natural, nonoxygenated lakes, trophic state and oxygen concentration of lake water and sediments are closely linked. First, high levels of primary production result in high dissolved oxygen (DO) consumption in the hypolimnion and a low penetration depth of oxygen into the sediment. Second, the DO concentration of the water overlaying the sediment affects the release of phosphorus (P) from the sediment: As Einsele (1936) proposed and Mortimer (1941) demonstrated in his classical field and laboratory studies, P is retained effectively in the sediment if the overlaying water is oxic but is released as soon as this water turns anoxic. Numerous field studies (e.g., Ashley 1983; Prepas and Burke 1997) have shown the reduction of hypolimnetic P concentrations after the onset of artificial oxygenation.

This interaction of P and DO has called for a combined approach when targeting eutrophication in Swiss lakes. On the Swiss Plateau (Fig. 1), a series of medium-sized lakes (up to 15 km<sup>2</sup>), embedded in intensively cultivated drainage basins, reached their eutrophication peaks in the 1970s and early 1980s (Fig. 2A) due to high input of P from wastewater (Fig. 2B). As a consequence of the lakes' high productivity, they are characterized by autochthonous sediments, i.e., by sedi-

ments largely consisting of organic material and calcium carbonate produced within the lake. Today, as the P input has been lowered significantly by sewage treatment plants with tertiary treatment for P removal, a higher share of the external input originates from agricultural soils. Despite the lower load, P concentrations of the lakes still range on the eutrophic level (40–90 mg m<sup>-3</sup> during spring overturn). Starting in the 1980s, three medium-sized lakes, in addition to several smaller lakes (not considered here), were equipped with aeration/oxygenation systems. Aeration is carried out during wintertime to facilitate convection and thereby increase oxygen transfer across the lake surface. During summer, oxygen is introduced into the hypolimnion of Sempachersee, Baldeggersee, and Hallwilersee to partially replace DO consumed by microorganisms degrading settling organic matter. These aeration and oxygenation systems sustain oxic habitats for fish and benthic organisms in the hypolimnion and, in part, at the sediment surface (Stössel 1987).

Though P input reduction and oxygenation measures have proven effective, it has, so far, been difficult to distinguish the effects on P retention between these two approaches. Within the past 15 yr, new evidence suggests a more complex picture of the P–DO relation than proposed by Einsele (1936) and Mortimer (1941). P retention in the sediment was found to be affected by changes in the physiology of sediment-dwelling bacteria that are able to increase P storage under oxic conditions (Gächter et al. 1988; Prepas and Burke 1997). In addition, several studies have demonstrated no increased sedimentary P retention due to aeration/oxygenation (e.g., Garrell et al. 1977; Gächter and Wehrli 1998).

As monitoring programs have been in effect for the Swiss Plateau lakes for 10–20 yr, long data series are now available that allow us to reevaluate the effects of DO and P concentrations on P retention and to assess the fundamental changes

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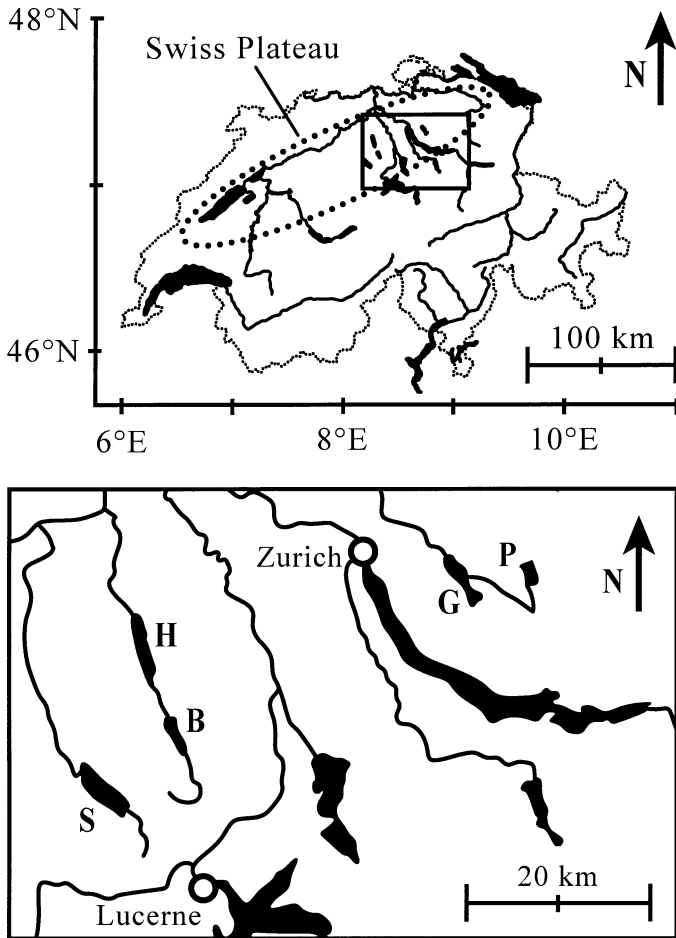


Fig. 1. Map of Switzerland. Detail shows the lakes studied. B, Baldeggersee; G, Greifensee; H, Hallwilersee; P, Pfäffikersee; S, Sempachersee.

in these lakes since their eutrophication peak. Furthermore, these new investigations are promising due to the fact that the P concentrations in these lakes have reached new near-steady levels in the 1990s, with much smaller year-to-year fluctuations than in the previous decades. This stable situation allows increased accuracy in P balances that was not possible to attain during the times of rapid increase and decline of P concentrations.

To single out the effect of oxygenation from the effect of P-load changes on P retention, two approaches are possible. In the first approach, a lake is monitored before and after the onset of aeration/oxygenation measures (e.g., Steinberg and Arzet 1984). However, data before the start of these measures are generally sparse, potentially causing bias. As Garrell et al. (1977) pointed out, if oxygenation measures coincide with or are preceded by rapid changes in external loads, alterations in the lake internal P balance may be masked.

As a second approach, lakes of similar morphologic, hydrologic, and chemical characteristics but with differences in oxia conditions may be compared. Nürnberg (1984) used data from more than 80 lakes—both with oxia and anoxia hypolimnia—to compare models for internal P loads. She showed that, for lakes with anoxia hypolimnia, models that

incorporate internal P loading proved most appropriate to predict P concentrations.

In order to compare the changes in P retention due to aeration/oxygenation for different lakes, a sound budget of P load, export, and content needs to be established. Data sets long enough to statistically compensate for the effect of annual variations are required, as well as a measure of P retention that is insensitive to morphologic or hydrologic specifics of the lakes.

For this paper, a comparison between several lakes is carried out using extensive data sets available from monitoring programs over the last 10 yr. Also, long-term data from sediment cores and historic measurements are combined to assess differences over the past decades. Besides the three aerated/oxygenated lakes introduced above, two lakes that develop anoxia hypolimnia during stagnation are investigated: Greifensee, where no aeration/oxygenation measures are carried out, and Pfäffikersee, which is aerated to increase mixing and therefore oxygen uptake in winter but still turns anoxia in the hypolimnia in summer (Table 1).

The quantity of central interest in such a comparison is P retention, i.e., the fraction of the external P load that is permanently retained in the lake's sediment. P retention can be defined differently by setting the system boundary. We distinguish between a management and a process approach.

In the management approach, the key question is how to manage P input from external sources in order not to exceed the retention capacity of the considered lake. Therefore, the external P load is of interest, and the system boundary is defined by the lake's drainage basin. Dillon and Rigler (1974) defined retention as the difference between P input and export, divided by P input. This ratio is also commonly used to describe retention of shallow lakes (e.g., Søndergaard et al. 1999) or wetlands (e.g., Novak et al. 2004). This parameter depends solely on measurements of input and output but not on lake-internal data. Given that the lake is in steady state with its external P load, i.e., if P content is constant, it is a measure of the lake-sediment P retention. In the steady-state case, the difference between P input and export is identical to net sedimentation (the amount of deposited P that remains permanently in the sediment), and retention is the ratio of net sedimentation to input.

An alternative measure of P retention uses the ratio of net sedimentation (introduced above) to gross sedimentation (the P flux from the epilimnia to the stratified deep water). This can be described as a process approach because it helps understanding lake-internal processes. In this case, the system boundary is the lake's boundary, and processes are of interest within the lake only.

In this contribution, we use both approaches to evaluate P retention. The following two hypotheses will be tested based on data from oxygenated and untreated Swiss Plateau lakes:

- P retention in oxygenated lakes is higher than P retention in lakes with anoxia hypolimnia.
- P retention during times of highest P concentrations is different from P retention in today's moderately eutrophic lakes.

The second hypothesis is easily testable due to the pro-

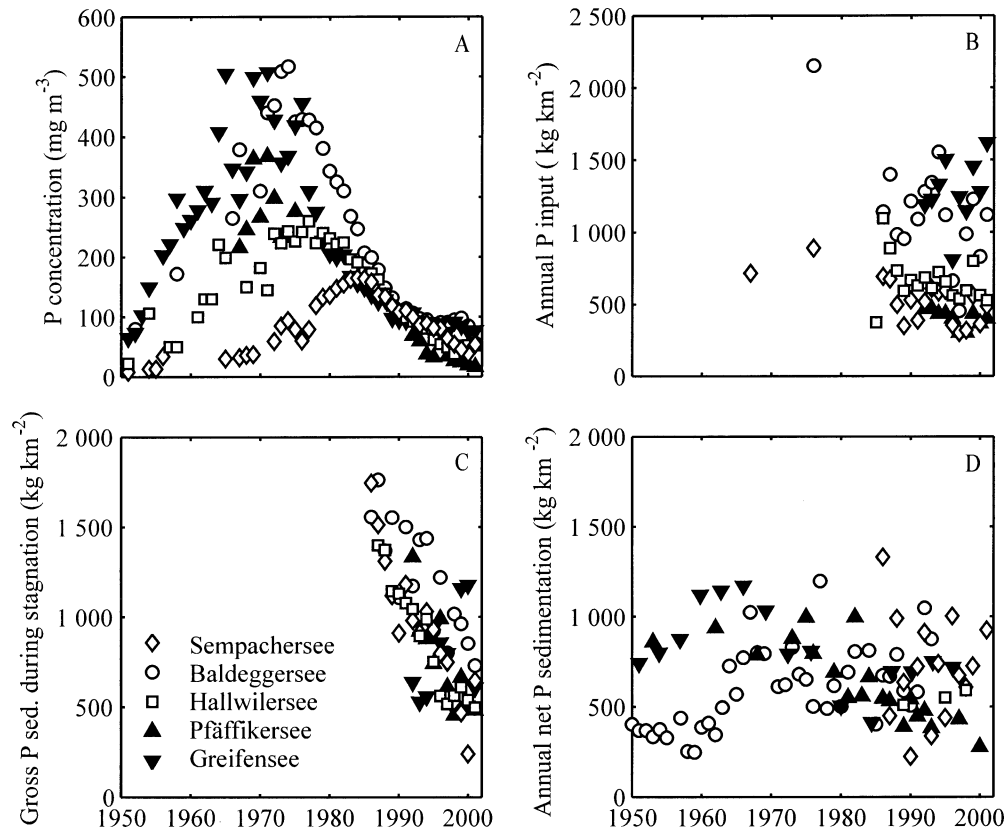


Fig. 2. (A) Mean lake P concentration during spring overturn (February–April). (B) Annual input of bioavailable P. (C) Gross-sedimentation during stagnation from internal P balances. (D) Annual net sedimentation of P, from sediment core analysis.

Table 1. Physical and hydrologic characteristics of the lakes studied, type of aeration/oxygenation measures, and monitoring programs.

	Sempachersee	Baldeggersee	Hallwilersee	Pfäffikersee	Greifensee
<b>Physical and hydrologic characteristics</b>					
Surface area ( $\text{km}^2$ )	14.4	5.2	10.2	3.0	8.4
Maximum depth (m)	87	66	47	35	32
Volume ( $10^6 \text{ m}^3$ )	639	173	285	59	148
Water residence time (yr)	15.3	4.0	3.9	2.1	1.2
Catchment area ( $\text{km}^2$ )	61	68	124	30	163
<b>Aeration/oxygenation</b>					
Type of aeration/oxygenation system	Compressed air for artificial mixing in winter/oxygenation in summer	Compressed air for artificial mixing in winter/oxygenation in summer	Compressed air for artificial mixing in winter/oxygenation in summer	Compressed air for artificial mixing in winter	None
Oxygen concentration in the hypolimnion (mean of annual lows 1992–2001) ( $\text{mg L}^{-1}$ )	4.8	3.4	2.1	0.0	0.0
<b>Monitoring programs</b>					
Tributary P concentration sampling	Concentration measurements every 22 d and during high-flow events	Concentration measurements every 22 d and during high-flow events	Measurements at varying intervals	Measurements at varying intervals	Weekly measurements of total P
Lake-internal P sampling	Monthly at intervals of 2.5–10 m	Monthly at intervals of 2.5–10 m	Monthly at intervals of 2.5–5 m	Monthly to bi-monthly at intervals of 2.5–5 m	Monthly at intervals of 1–2.5 m

Table 2. P balance terms and errors for the period from 1992 to 2001 and for the period of highest P concentrations (hypertrophic period). Errors denote two standard deviations and are based on the variance of the data points (concentration and stream input), on estimates (sewage input, deposition, export, and net sedimentation from sediment cores), and on uncertainty calculations assuming Gaussian error distribution for independent variables (content change, gross sedimentation, net sedimentation from internal balance). NA, data not available.

	Sempachersee	Baldeggersee	Hallwilersee	Pfäffikersee	Greifensee
Eutrophic period	1992–2001	1992–2001	1992–2001	1992–2001	1992–2001
Concentration at spring overturn ( $\text{mg m}^{-3}$ )	$69 \pm 7$	$90 \pm 9$	$61 \pm 6$	$38 \pm 4$	$87 \pm 9$
Annual stream input ( $10^3 \text{ kg}$ )	$4.5 \pm 1.0$	$4.5 \pm 0.9$	$5.2 \pm 1.6$	$1.3 \pm 0.6$	$9.1 \pm 2.5$
Annual sewage input ( $10^3 \text{ kg}$ )	$0.5 \pm 0.1$	$0.7 \pm 0.1$	$0.4 \pm 0.04$	$0.2 \pm 0.1$	$0.8 \pm 0.1$
Annual deposition ( $10^3 \text{ kg}$ )	$1.3 \pm 0.7$	$0.3 \pm 0.1$	$0.8 \pm 0.4$	$0.2 \pm 0.1$	$0.9 \pm 0.4$
Annual total input ( $10^3 \text{ kg}$ )	$6.4 \pm 1.2$	$5.5 \pm 0.9$	$6.4 \pm 1.6$	$1.7 \pm 0.7$	$10.8 \pm 2.6$
Annual export ( $10^3 \text{ kg}$ )	$1.8 \pm 0.4$	$2.5 \pm 0.5$	$3.4 \pm 1.0$	$0.6 \pm 0.2$	$6.6 \pm 2.0$
Annual content change ( $10^3 \text{ kg}$ )	$-4.0 \pm 2.1$	$-0.9 \pm 0.7$	$-1.0 \pm 0.8$	$-0.3 \pm 0.1$	$-0.3 \pm 0.6$
Gross sedimentation during stagnation ( $10^3 \text{ kg}$ )	$10.5 \pm 0.5$	$5.5 \pm 0.3$	$7.1 \pm 0.7$	$1.6 \pm 0.2$	$6.5 \pm 0.7$
Annual net sedimentation from internal balance ( $10^3 \text{ kg}$ )	$8.6 \pm 1.2$	$3.9 \pm 0.5$	$4.0 \pm 0.8$	$0.9 \pm 0.2$	NA
Annual net sedimentation from sediment core ( $10^3 \text{ kg}$ )	NA	NA	$4.5 \pm 1.4$	$0.9 \pm 0.4$	$4.5 \pm 0.9$
Hypertrophic period	1984–1988	1971–1977	1972–1980	1967–1975	1969–1975
Concentration at spring overturn ( $\text{mg m}^{-3}$ )	$147 \pm 15$	$457 \pm 46$	$237 \pm 47$	$278 \pm 28$	$434 \pm 43$
Annual stream input ( $10^3 \text{ kg}$ )	$6.8 \pm 1.1$	$2.7 \pm 1.3$	NA	NA	NA
Annual sewage input ( $10^3 \text{ kg}$ )	$0.7 \pm 0.1$	$8.3 \pm 4.2$	NA	NA	NA
Annual deposition ( $10^3 \text{ kg}$ )	$1.4 \pm 0.7$	$0.2 \pm 0.1$	NA	NA	NA
Annual total input ( $10^3 \text{ kg}$ )	$8.9 \pm 1.3$	$11.2 \pm 4.4$	$14.6 \pm 7.3$	$6.8 \pm 3.4$	$42.7 \pm 21.4$
Annual export ( $10^3 \text{ kg}$ )	$4.2 \pm 0.8$	$6.8 \pm 1.4$	$10.8 \pm 5.4$	$4.9 \pm 1.5$	$38.8 \pm 11.6$
Annual content change ( $10^3 \text{ kg}$ )	$-4.8 \pm 3.3$	$-0.6 \pm 4.1$	$-0.7 \pm 6.8$	$0.4 \pm 0.8$	$-0.9 \pm 3.7$
Gross sedimentation during stagnation ( $10^3 \text{ kg}$ )	$23.2 \pm 2.0$	$10.2 \pm 2.2$	$20.1 \pm 2.2$	$4.8 \pm 1.0$	$19.9 \pm 5.9$
Annual net sedimentation from internal balance ( $10^3 \text{ kg}$ )	$9.6 \pm 3.8$	$5.0 \pm 3.3$	$4.4 \pm 3.4$	$1.4 \pm 1.5$	NA
Annual net sedimentation from sediment core ( $10^3 \text{ kg}$ )	NA	$3.8 \pm 1.1$	$3.3 \pm 1.7$	$1.6 \pm 0.5$	$4.9 \pm 1.0$

nounced changes in P concentrations in these lakes during the past decades.

## Database

For the present study, five medium-sized eutrophic lakes, situated on the Swiss Plateau, were selected (Fig. 1). Table 1 shows their physical and hydrological characteristics and the type of aeration/oxygenation measures applied. For each of these lakes, data sets of P input, content, and export measurements are available for a period of at least 10 yr (Stadelmann et al. 2002; Butscher, Environmental Agency of Canton Lucerne, unpubl. data; Niederhauser, Environmental Agency of Canton Zurich, unpubl.; Stöckli, Environmental Agency of Canton Aargau, unpubl. data). The sampling procedure for Sempachersee and Baldeggersee is detailed in Gächter and Wehrli (1998). Specifics for the other lakes are described below. The period from 1992 to 2001 was selected for the comparison of these lakes. Over this period, detailed data are available for all lakes; and unlike during earlier periods, P input, concentration, and net sedimentation data were rather constant, allowing reliable averaging. For the times of highest P concentration, less detailed data are available. Periods of 5–9 yr, specific for each lake, were selected

(Table 2), during which P concentrations remained relatively constant, and average values of input and export were used.

P inputs include streams, wastewater from treatment plants, and atmospheric deposition. The sampling strategy for the different catchments is characterized in Table 1. Input from wastewater treatment plants was determined from routine sampling and storm-overflow sampling. For atmospheric P deposition, an average rainwater concentration value of  $83 \text{ mg m}^{-3}$  was estimated for all lakes (Scharrer et al. 1951; Krummenacher 1976). This amounted to deposition values in the range of  $70\text{--}110 \text{ kg km}^{-2} \text{ yr}^{-1}$ . Input data errors were determined from measurement variances (stream data) or estimated (sewage input and deposition).

The stream input of dissolved P was considered to be bioavailable, whereas pedogeneous particulate P was assumed to settle near the inlets, without participating in the lake's internal P cycling. However, in streams originating from other lakes, total P was assumed bioavailable because most particulate P was incorporated in algal biomass. For Hallwilersee and Pfäffikersee, inputs were not measured during the whole period considered here. This leads to larger uncertainties of these values (see Table 2).

Total P concentration in the water column was analyzed in approximately monthly intervals at the deepest locations



of the lakes. P content was determined by integrating concentrations over the depth-dependent cross-sectional areas. Sampling depth intervals are summarized in Table 1. The error in P contents was determined from reproducibility of P concentration measurements and the estimated error of depth interpolation.

P output was calculated from linearly interpolated surface P concentrations in the lakes (average of concentrations from 0- to 2.5-m depth), multiplied by discharge measured daily in the outlet rivers. The output data uncertainty consists of errors in the concentration measurements, the discharge measurement, and interpolation error.

Annual P net sedimentation was determined from P concentrations and bulk sedimentation rates in dated sediment cores, as described by Lotter et al. (1997). Net sedimentation for the balance was obtained by multiplying the locally determined net sedimentation by the area of the lake's hypolimnion. For the time periods considered, only one sediment core per lake was available. Errors due to spatial variation were estimated from observed variations in P concentrations in sediment surface samples collected at different locations in Sempachersee (Sturm 1993) and Greifensee (H. Bühner, EAWAG, unpubl. data). In addition, analytical errors and estimated errors of the sedimentation rate were considered.

### Budgeting concept

Besides using sediment data, annual net sedimentation  $N$  (kg) can be determined from the internal phosphorus balance,

$$N = -\Delta P + I - O \text{ (kg)} \quad (1)$$

where  $\Delta P$  is the change in total P content of the water column in (kg) over the period of 1 yr,  $I$  is the annual input of bioavailable P (kg), and  $O$  is the annual output of total P (kg) via the outlet river.

The change in total P content,  $\Delta P$ , was calculated based on the mean content at the end of winter circulation. These mean values were calculated using profiles measured between 1 February and 30 April of each year. This period was chosen because P content was mostly constant during that time and substantial P sedimentation from the epilimnion had not yet set in.

Gross sedimentation  $G$  for all lakes was calculated using the internal balance,

$$G = -\Delta P_{\text{stag}} + I_{\text{stag}} - O_{\text{stag}} \text{ (kg)} \quad (2)$$

where  $\Delta P_{\text{stag}}$  is the change in P content of the epilimnion in (kg),  $I_{\text{stag}}$  is the input of bioavailable P (kg), and  $O_{\text{stag}}$  is the output of total P (kg) via the outlet, each during the stagnation period. The interval from 01 April to 31 October was considered as the stagnation period, and the epilimnion depth was defined as the depth down to which total P was completely mixed by 31 October in all years. It ranged between 11 and 16.5 m for the lakes studied.

Gross sedimentation can be calculated from an internal balance during stagnation only, when turbulent mixing of P from the deep water to the epilimnion is negligible compared with  $I_{\text{stag}}$  (Wüest and Lorke 2003). In this article, gross sedimentation during stagnation calculated from the internal

balance will be used. Sediment trap studies for Sempachersee (Gächter and Meyer 1990) and Greifensee (Sturm, EAWAG, unpubl. data) show that these values for gross sedimentation during stagnation agree well with the settling P collected in sediment traps over the same period and typically amount to 70% of the annual gross sedimentation.

Annual net sedimentation,  $N$ , annual input,  $I$ , and gross sedimentation,  $G$  (during stagnation), were used to calculate the two measures of retention,  $R_1$  and  $R_2$ , where  $R_1 = N/I$  (management approach) and  $R_2 = N/G$  (process approach).

### Results

Figure 2A shows a steep increase of P concentrations in all lakes starting in the 1950s and 1960s and a similarly steep decrease, which largely occurred in the 1980s. P input data before 1985 is very sparse (Fig. 2B), but suggests a reduction in P input for Sempachersee and Baldeggersee between the 1970s and 1980s. Time series of gross and net sedimentation are shown in Fig. 2C,D. Input and gross and net sedimentation fluctuate due to natural variations and measurement precision. Average values and their standard errors are summarized in Table 2. Where net sedimentation was obtained both from the internal balance (Eq. 1) and from sediment cores, the agreement is well within the margins of errors. In most situations, gross sedimentation during stagnation is close to total annual input. These high values of gross sedimentation can be explained by internal loading (P flux from the sediment back into the water column), increasing the P content of the water column and subsequently contributing to gross sedimentation. In addition, the large value of gross sedimentation in Sempachersee is due to the fact that it is not yet in steady state, i.e., content and gross sedimentation are still decreasing over time (Fig. 2A,C).

The retention terms,  $R_1$  and  $R_2$ , averaged over the period of 1992–2001, are shown in Fig. 3A. The term  $R_1$  (net sedimentation/input) is meaningful only under near-steady-state conditions. As Sempachersee did not yet reach a complete steady state due to its long residence time (Table 1),  $R_1$  is larger than one for this lake. In Baldeggersee, Hallwilersee, and Pfäffikersee, the  $R_1$  values are identical within the margins of error.

Problems of nonsteady states and long residence times are avoided when using  $R_2$ . Figure 3B shows that this measure of retention is identical within the margins of error in all lakes. As Fig. 3A,B shows, there is no statistically significant difference between P retention  $R_1$  and  $R_2$  in lakes with oxic and anoxic hypolimnia, respectively. Therefore, hypothesis (a)—that P retention in oxygenated lakes is different from P retention in lakes with anoxic hypolimnia—is not supported by our data.

To test hypothesis (b)—that P retention at highest P concentrations is different from P retention in moderately eutrophic lakes— $R_1$  and  $R_2$  values of the periods when P concentrations were at their maximum ( $>100 \text{ mg m}^{-3}$ ; hypertrophic state, see figure caption for years) are compared with the values observed from 1992 to 2001. As shown in Fig. 4, both retention measures are higher in the later period for all lakes. Significant differences ( $p = 0.05$ ) between the two

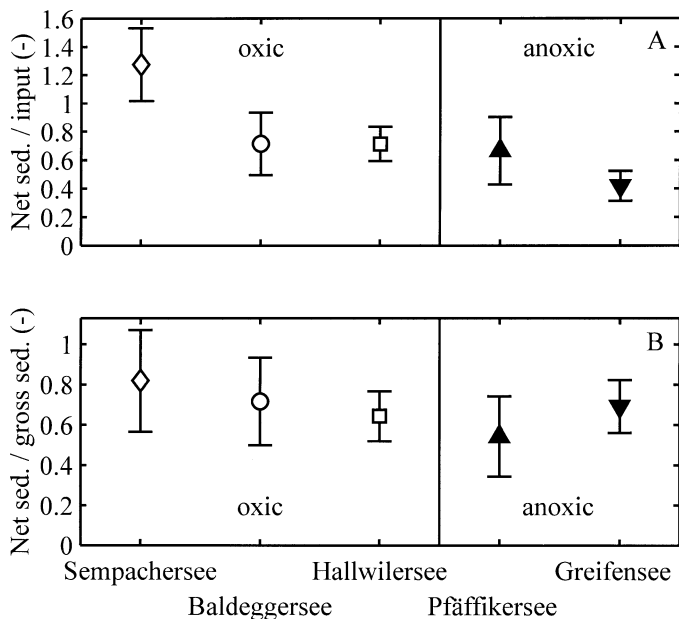


Fig. 3. (A) Retention  $R_1$  as ratio of average net sedimentation to average input. (B) Retention  $R_2$  as ratio of average annual net sedimentation to average gross sedimentation during stagnation. The error bars denote two standard deviations calculated from the errors in the phosphorus balance terms (Table 2). Period used for averaging: 1992–2001. Sempachersee, Baldeggersee, and Hallwilersee are oxic lakes; Pfäffikersee and Greifensee develop an anoxic hypolimnion during summer stagnation.

periods can be found for the following lakes: Baldeggersee ( $R_1$  and  $R_2$ ), Hallwilersee ( $R_1$  and  $R_2$ ), Greifensee ( $R_1$  and  $R_2$ ), Pfäffikersee ( $R_1$  only). Therefore, in both oxygenated lakes and lakes with anoxic hypolimnion, retention  $R_1$  and  $R_2$  has increased substantially since the time of maximum P concentration.

## Discussion

Obviously, retention as defined here is inherently dependent on the trophic state of a lake:  $R_1$  is a function of input (which was higher in all investigated lakes during the time of maximum concentration), and  $R_2$  is a function of gross sedimentation, which is also higher if more P is available to be incorporated into settling biomass. The dependence of  $R_1$  and  $R_2$  on the P concentration can be illustrated further by plotting  $R_1$  and  $R_2$  against average P concentrations,  $[P]$ , in the water column (Fig. 5). Notwithstanding the large errors of the single data points, the present data indicate an inverse relationship between  $[P]$  and the measures of retention,  $R_1$  and  $R_2$ ,

$$R_1 = N/I = (36 \text{ mg m}^{-3})/[P] \quad (3)$$

$$R_2 = N/G = (39 \text{ mg m}^{-3})/[P] \quad (4)$$

It is important to stress that the errors of these least-square fits are large (the average residuals of  $R_1$  and  $R_2$  are 0.15 and 0.20, respectively), and the fits are very sensitive to the data points with low P concentration values. An inverse relationship suggests that (a)  $[P]$  is proportional to input  $I$  (Eq. 3) and  $[P]$  is proportional to gross sedimentation  $G$  (Eq. 4) for all lakes,

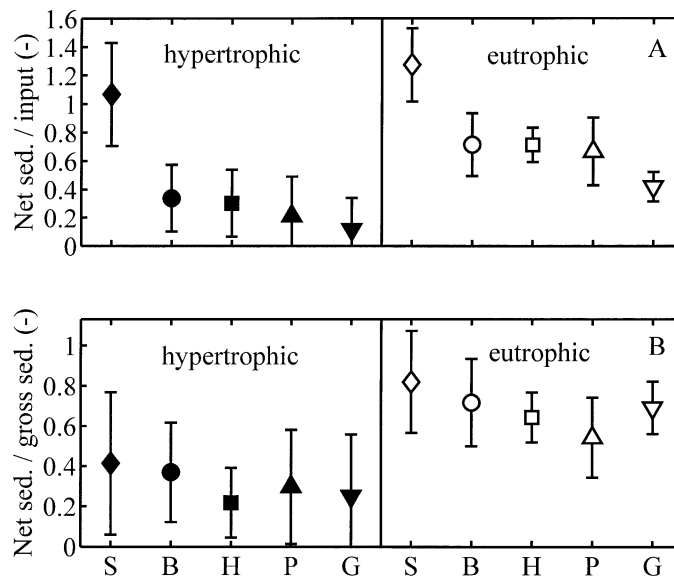


Fig. 4. (A) Retention  $R_1$  as ratio of net sedimentation to input. (B) Retention  $R_2$  as ratio of annual net sedimentation to gross sedimentation during stagnation. Error bars denote two standard deviations calculated from errors in the phosphorus balance terms (Table 2). The values represented by black symbols were calculated for the periods of highest P concentrations (hypertrophic state). These periods are 1984–1988 for Sempachersee, 1971–1977 for Baldeggersee, 1972–1980 for Hallwilersee, 1967–1975 for Pfäffikersee, and 1969–1975 for Greifensee.

and (b) net sedimentation  $N$  is constant and independent of  $[P]$ . The lake that deviates most from the inverse relationship is Baldeggersee, which exhibited moderate values of  $G$  and  $I$  despite very high P concentrations in the 1970s (Table 2). This can be attributed to an underestimation of  $I$  during this period, where only occasional input data exist.

Proportionality between gross sedimentation and the amount of epilimnic P originates from its availability to algae, which export P from the epilimnion into the deep waters of the lakes. However, at very high epilimnic  $[P]$ , assimilation and, thus, gross sedimentation are limited by light penetration rather than by available nutrients.

As Fig. 6 shows, net sedimentation is indeed similar in all lakes in both periods: Annual net sedimentation ranges between 280 and 950  $\text{kg km}^{-2} \text{ yr}^{-1}$ , with no significant differences between groups of lakes or trophic states. At one point, however,  $N$  must decrease if  $[P]$  decreases below a not yet defined  $[P_{\text{crit}}]$ , because, in steady state,  $N$  cannot exceed  $G$  or  $I$ . This seems not yet to be the case in the lakes studied here, because P concentrations are still relatively high ( $\geq 38 \text{ mg m}^{-3}$ , Table 1). According to Eq. (3)—in a hypothetical average lake— $[P_{\text{crit}}]$  can be expected at about  $36 \text{ mg m}^{-3}$ . Of course, individual lakes may deviate from this value.

The finding that net sedimentation has an upper limit, independent of trophic state and DO concentration in the lake water, may be attributed to the following process: In eutrophic lakes, oxygen penetrates only a very thin layer at the sediment surface. Due to the large pool of reduced material in the sediment and the diffusive boundary layer, oxygen is

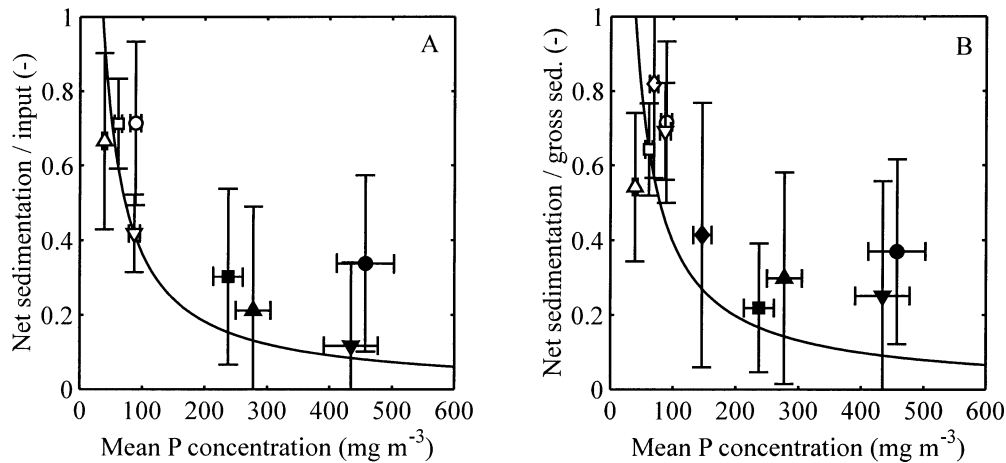


Fig. 5. Measures of retention (A)  $R_1$  and (B)  $R_2$  versus mean P concentration at spring overturn. The symbols for the lakes (definition in Fig. 2) are the same as in Figs. 2–4. Sempachersee is omitted in A because  $R_1 > 1$  (nonsteady state, see Fig. 4). Black symbols denote periods of highest P concentrations, as in Fig. 4. Open symbols denote the period of 1992–2001. The curves show a least-square fit to the data points, using an inverse relationship.

consumed at the sediment surface, resulting in still anoxic sediments in deeper strata (Müller et al. 2002; Lorke et al. 2003). In addition, seasonal biogenic calcite precipitation forms sediment layers of several millimeters that may not adsorb much P (Hupfer et al. 2000) but that act as a diffusion barrier between sediment and water, further inhibiting downward penetration of DO. Anoxic sediments, however, do not necessarily mean that inorganic P is liberated entirely from the sediment. Due to high local activities of Fe(II) and P, vivianite or some amorphous mixed Fe(II)- $\text{PO}_4$ -hydroxide may be precipitated. Fe(II)-bound P may be released when high sulfate concentrations are reduced, and S(-II) competes with P for Fe(II) (Gächter and Müller 2003).

The finding that net sedimentation rates are not only similar in oxic and anoxic conditions but also between different lakes may be attributed to the comparable geology of their catchments, resulting in similar composition of the lake sediment. We speculate that net sedimentation in anoxic sedi-

ments may depend on the input of minerals like Fe and Ca and the ratio of this input to the sediment area, which does not vary extensively in the lakes studied. Of course, an analysis of the actual mineral inputs is necessary to investigate this point further.

Another difference between the five lakes that did not affect net sedimentation is their eutrophication history. Sediment core analysis shows that the lakes' sediments turned anoxic at different times between the years of 1885 (Baldeggersee; Lotter et al. 1997) and 1936 (Sempachersee; Sturm 1993). However, this does not affect present net sedimentation because net sedimentation is controlled by processes at the sediment surface, not by the depth of the anoxic sediment layer.

When studying mass balances in systems characterized by high natural fluctuations and measurement uncertainties, errors have to be assessed critically. Especially, the following complications have to be considered: (a) input P loads are laborious to quantify and vary from year to year because of their strong dependence on water discharge (e.g., Cohn 1995); (b) depending on the speciation, an unknown fraction of the imported particulate P may be bioavailable; and (c) artificial circulation slightly increases the export because of more efficient and prolonged vertical homogenization of P during winter convection. The effects of these three processes can be regarded as minor for the data presented because (a) a combination of lake-external, lake-internal, and sediment data was used, which allowed establishing balances independent of relatively inaccurate input estimates; (b) net sedimentation  $N$  from sediment core data and  $N$  from the internal balances (Eq. 1) agree best, assuming that particulate P load is not bioavailable; and (c) the increase of P export due to prolonged winter convection was found to be small compared with the overall P export error.

Net sedimentation from internal balances contains relatively large errors, mainly due to natural variations of input and seasonal variations of P content (Table 2). Therefore, we

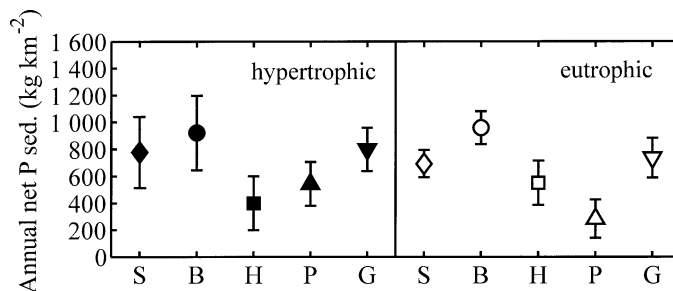


Fig. 6. Average annual net sedimentation. Black symbols denote periods of highest P concentrations, as in Fig. 4. Open symbols denote the period of 1992–2001. For Sempachersee and Baldeggersee, 1992–2001, net sedimentation was calculated from the internal balance. For the other periods and lakes, net sedimentation was calculated from sediment core data. Error bars denote two standard deviations and the estimated error of the sediment core data, respectively.

Table 3. Average iron and phosphorus concentrations and their ratios in lake sediments. For groups of lakes, maximum and minimum values are shown.

Lake	Fe concentration [mg Fe g <sup>-1</sup> ]	P concentration [mg P g <sup>-1</sup> ]	Fe/P (mass)	Fe/P (molar)
Swiss Plateau lakes				
Sempachersee, sediment depth 0–5 cm*	16.6±2.0	1.5±1.3	11.1	6.1
Hallwilersee, sediment depth 0–5 cm†	7.2±0.7	0.7±0.1	10.2	5.7
Mesotrophic Swiss lakes				
Lake Constance, sediment depth 0–2.5 cm‡	15.8±2.2	0.2±0.1	79.0	43.9
Lake Zurich, sediment depth 0–2.5 cm‡	4.3±0.7	0.4±0.1	11.9	6.6
Groups of lakes				
15 Danish lakes, sediment depth 0–5 cm§	5.7–159	0.4–6.8	1.8–61.7	1.0–45.4
16 lakes in northwestern Ontario, sediment depth 0–20 cm	14.5–90.3	2.0–6.6	4.6–15.4	2.4–8.5

\* Gächter and Meier (1990).

† Stöckli, Environmental Agency of Canton Aargau, unpubl. data.

‡ Züllig (1956).

§ Jensen et al. (1992).

|| Brunskill et al. (1971).

suggest that, for a proper balance, net sedimentation should be determined from the P burial in dated sediment cores rather than from external fluxes. Dillon and Evans (1993) compared retention obtained from P balances and from sediment cores. They concluded that P retention calculated from sediment cores may be a suitable alternative to a mass-balance approach, provided that accurate sediment accumulation rates can be obtained and that several cores are collected from the lake. The shortcoming of the present study, that only one dated sediment core was available for each lake, is accounted for by the higher errors of net sedimentation (Table 2). Still, net sedimentation determined from sediment cores and internal balances are surprisingly close and well within the margins of error (Table 2).

From the analysis of the presented long-term data sets, we conclude that averaging over a period of 5–10 yr is typically necessary to establish P budgets with acceptable accuracy.

The retention measures,  $R_1$  and  $R_2$ , were introduced to represent a management and a process perspective. From the management perspective, one can conclude from Fig. 3A that, in lakes of the Swiss Plateau, oxygenation did not help retain a larger fraction of the P introduced into these lakes. Nevertheless, oxygenation/aeration is an important lake management measure, as it enlarges the oxic habitat for fish and benthic organisms, as was shown for the oxygenated lakes discussed here (Stössel 1987; Stadelmann et al. 2002). Benthic organisms may also accelerate decomposition of organic matter and mobilization of phosphorus at the sediment surface and therefore mask an expected increased benthic P retention due to an increased redox potential. However, as our data show, the two effects are either small or cancel out within the margins of error. In conclusion, oxygenation/aeration is a valid measure to improve the ecological state of a lake but cannot substitute for a decrease of the external P loading (Gächter 1987).

From the process perspective, one can conclude that the main limiting factor of P uptake in the sediments of the Swiss Plateau lakes is the threshold of net sedimentation that

depends on the mineralization rate of settling organic matter, the availability and/or formation of P-binding minerals in the sediment, and the mobility of dissolved P in the sediment, which is influenced by the sedimentation rate and the penetration depth of oxygen. Therefore, the findings discussed here may not be applicable to all types of lakes. Swiss Plateau lakes are characterized by autochthonous sediments with relatively low Fe/P ratios (see Table 3). Jensen et al. (1992) found that lake sediments with Fe/P ratios exceeding 15 (by mass) released less soluble reactive phosphorus (SRP) under aerobic conditions, whereas sediments with Fe/P ratios below 10 showed no correlation between Fe/P ratios and SRP release rates. The lakes studied here can be attributed to the latter category. In addition to autochthonous sediments, sediments of mainly external origin may also exhibit low Fe/P ratios, as shown for the sediments of oligotrophic lakes in northwestern Ontario (Table 3; Brunskill et al. 1971). For such lakes, we can also expect that P retention is controlled by the composition of the sediment rather than by the oxic state of the water overlaying the sediment.

As Fe concentrations in the lake sediments seem to control benthic P retention of the Swiss Plateau Lakes, Fe or Al addition might be considered to increase their P retention. Effects of such measures on a small lake are discussed by Hansen et al. (2003). In the lakes studied here, these measures do not seem feasible due to the size of the lakes and the still substantial P input, which would require repeated addition of Fe. It is also important to note that of any amount of Fe added, a substantial part would react with sulfide present in the sediment. For Sempachersee, Urban et al. (1997) showed that sulfate reduction equaled about 50% (molar) of the Fe fluxes across the sediment.

How can eutrophic, aerated lakes be classified in a scheme of oxic and anoxic lakes, as it was used by Nürnberg (1984)? In most cases, an oxic hypolimnion coincides with oligo- and mesotrophy, while anoxic conditions in the hypolimnion coincide with eutrophy. For the lakes of the Swiss Plateau, we showed that, with respect to P retention, oxygenated



lakes still fit into the category of anoxic, eutrophic lakes. Even though their hypolimnion is oxic, retention is low due to their still eutrophic status and anoxic sediments. We thus conclude that P concentration in the lake water, rather than hypolimnetic concentration of dissolved oxygen, determines P retention in these lakes.

The finding that net sedimentation has an upper limit is important for lake and catchment management: When concentration [P] exceeds  $[P_{crit}]$  (around  $40 \text{ mg m}^{-3}$  in the lakes studied here), the relationship between input ( $I$ ) and [P] deviates from linearity. In other words, a further increase of  $I$  causes an actual decrease of P retention (defined as  $N/I$ ), and hence, results in an accelerated increase of [P]. On the other hand, input reduction measures may lead to a more efficient P removal once the lake P concentration has been lowered to  $[P_{crit}]$ . However, at which point  $[P_{crit}]$  will be reached in a specific lake is uncertain. Detailed long-term monitoring, which will continue in all five lakes, may help detect such an effect, provided that P contents continue to decrease in the coming years.

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