

## ***Interactive comment on* “The influences of historic lake trophy and mixing regime changes on long-term phosphorus fractions retention in sediments of deep, eutrophic lakes: a case study from Lake Burgäschi, Switzerland” by Luyao Tu et al.**

### **Anonymous Referee #1**

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General comments: This is a very careful and detailed state-of-the-art case study of the trophic history of a small Swiss lake (Burgäschisee) exclusively from the analysis of a single sediment core. The authors present an interesting data set that deserves, however, a more deepened discussion and a more complete and careful presentation. More than 50 years ago, lake managers hypothesized based on water column P mass balance considerations that hypolimnetic water withdrawal must result in a decreasing sediment P content. Apart from confirming this prediction, the MS – in its present state

– contributes little to a better understanding of the benthic P cycling. Moreover, I have some reservations in terms of interpretation of in-lake processes and suggest some points to be revised. In fact, the interpretation of the data in the context of sediment diagenesis and processes in the water column (chapter 5.3. onwards) is not consistent. Some statements have no foundations in the results. The discussion contains several contradictions and, therefore, inaccurate conclusions. A wealth of data have been produced from this sediment core but little of it was used to interpret biogeochemical processes in the lake and its sediment. The effects of deep water syphoning starting 1977 is not considered appropriately for the interpretation of sediment profiles and biogeochemical lake processes. The manuscript could be significantly improved and made more attractive for a broader readership if the processes of P scavenging were better characterized (data permitting). The manuscript should be revised aiming to develop a straightforward concept easily explaining benthic P retention as a result of gross P sedimentation, redox dependent benthic transformation and inorganic P sequestration, transient periodic P accumulation in the hypolimnion and P export due to hypolimnetic water withdrawal. Specific points are discussed below.

Specific comments: Lines 65/66: You might wish to replace the sentence “However, the long term influence . . . . . “ by the following information: Gächter (1976, Die Tiefenwasserableitung, ein Weg zur Sanierung von Seen. Schweiz. Z. Hydrol. 38: 1-28.) demonstrated that syphoning of hypolimnetic water affects the seasonal lake internal P cycling as follows: 1. P released from sediments during anoxia does not accumulate in the hypolimnion because it is efficiently exported out of the lake, and 2. hence, cannot re-precipitate and settle again to the sediment during spring overturn. 3. Consequently, hypolimnetic withdrawal must result in a phosphorus impoverishment of the sediment and 4. thus, – in the long term – very likely in a decreasing benthic P release during summer stagnation.

Line 165ff: For your further interpretation of the trophic state of the lake it is essential to document whether green pigments preserve well in the sediments over decades. To

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my knowledge, the chlorin index (Schubert et al., 2005, *Geochem. Geophys. Geosys.* 6, 3) that traces chlorophyll and degradation products, increases quite fast downcore (indicating decomposition of chlorophylls).

Line 177: According to your extraction scheme, you determined five operationally defined P fractions (F1 to F4 and the total P). Which fraction represents the refractory organic P? Is it defined as  $TP - (F1+F2+F3+F4)$ ?

Line 274: “Afterwards” is confusing, because sediment age decreases downwards. Suggestion: Replace “Afterwards” by “then, with decreasing age, they increase . . . .”

Line 280: I suggest to extend Fig. 5 by inserting a profile of the annual total P (TP) retention equaling TP content x MAR and to briefly describe its characteristics here. (see also comment to Lines 311 ff.). For the interpretation of sedimentary processes it might be helpful to present other parameters in amount per area per time (areal mass accumulation rate) as well.

Line 291: Unless it has been shown that “green pigments” behave absolutely refractory (i.e., that they do not degrade with increasing age after deposition), I doubt that it is save to interpret their profile uncritically as an indicator for the lake’s productivity at the time when the pigment was buried in the sediment.

Line 292: Delete ‘with each other’.

Lines 295 to 297: See comment to line 291

Line 304 ff.: 1943 the lake water level and hence the water table level was artificially lowered by more than 2 m in order to create more crop land (see Guthruf et al, 1999). Discuss the possible effect of this measure on the nutrient load of the lake. It is surprising that this measure is not immediately visible in the sediment profiles and MARs. However, as sedimentation rates are different in the two cores analyzed (Figure 2c), the year 1943 can be located at ~40 cm or at ~50 cm sediment depth, which allows quite a range for indicators to look for.

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Lines 311 ff.: Fig. 4 provides semi quantitative information about the sediment content of the presented elements that should not be misinterpreted as their more informative annual net-deposition rates (gross deposition minus release). This information could be obtained for TIC and the various phosphorus species by simultaneous consideration of MAR (Fig. 2c) and the information on the corresponding sediment content (Fig. 5).

Line 332-33: I would assume that Fe and Mn in the sediment have their source and continuous supply in the catchment. The pattern is caused by bottom water anoxia, sediment diagenetic processes, and physical mixing processes (given that the deposition of organic matter exceeds the critical threshold. Since laminated Fe/Mn patterns appear already before 1926 I assume that this threshold was exceeded already then, and bottom water anoxia was common during the stratified season?).

Line 355ff: From the Fe/Mn pattern in the sediment one can conclude on the oxygen conditions in the hypolimnion, i.e. physical mixing. It is, however, difficult to conclude on primary productivity. PP attains a maximum (in terms of assimilated carbon) at relatively low phosphorus concentration and does not increase with P ad infinitum. The same is true for O<sub>2</sub> consumption in the hypolimnion, which reaches a maximum rate of  $\sim 1.1$  g O<sub>2</sub> m<sup>-2</sup>d<sup>-1</sup> for productive lakes. Moreover, the O<sub>2</sub> reservoir of a lake with a small hypolimnion volume as Burgäschisee is used up very quickly, and is thus naturally very sensitive to increasing primary production.

Line 362: Replace “no” by “absent”

Line 373 ff.: According to the P extraction scheme, Ca-bound P would most likely dissolve as HCl-TP (provided that most of the HCl-TP is inorganic P). As the HCl-TP content does not systematically change within Zone IV but MAR decreases with decreasing sediment age, the presented data do not support the conclusion that a changing environment resulted in an increasing rate of benthic Ca-bound P burial. In fact, the annual deposition rate of Ca-bound P [amount per area per time] decreases.

It is not comprehensible that P-coprecipitation with calcite predominates after 1977 “as

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an incidence of biologically driven precipitation . . . in highly productive lakes” because the lake was highly productive for decades. My guess is that this clear pattern in the sediment is an effect of the deep water siphoning that was installed at that time, which removed not only hypolimnetic P but also dissolved Fe and Mn, leaving calcite as the main sorbent for P? The installation of the syphoning facility and its effect on the biogeochemistry of the lake must be included in the discussion! It has affected lake processes fundamentally, and the new patterns can only be interpreted when the consequences of the syphoning are considered.

Line 382ff: Replace “covering” by “covering” The first sentence is too general as it refers to the whole core. At least in zone IV it is obvious that P retention is mainly due to biogenic calcite formation.

Line 383: The Fe/Ti ratio indicates allochthonous Fe, not autochthonous? In fact, all Fe and Mn originates from the catchment, and the formation of Fe(II) and Mn(II) is a sediment diagenetic process leading to co-precipitation of P during mixing with oxygenated water masses.

Line 383-387: Here you assume that all sediment-P is bound to Fe(III) and Mn(IV) phases. However, at least in zone III, there was a high amount of NaOH-P in addition to NaBD-P indicating that a substantial amount of P was not bound to reducible Fe(III) phases. What is the binding form here? Could it possibly (partly) consist of precipitates of Fe(II)-phosphate or similar? Do you have geochemical indicators to separate Fe(II) from Fe(III) in the sediment?

Line 387-388: “. . . when the hypolimnion had better oxic conditions. . .”. What is the base for this assumption? The lakes bottom water during stratification was anoxic already before 1926 (Mn-Fe rich laminations, Figure 3) and productivity even increased afterwards (paragraph line 304, paragraph line 311, paragraph line 346 (‘stable anoxic hypolimnetic waters’ in zone II), etc.).

Line 393: contradiction: ‘Mn and Fe oxyhydroxides’ are not ‘reduced P-bearing solid

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phases’.

Line 394: What are ‘more anoxic conditions’? Conditions are either oxic or anoxic.

Line 394-395: The effect of hypolimnetic syphoning must be taken into consideration here.

Line 397-399: ‘... reduced Mn and Fe preservation suggests ...’ Do you suggest that Fe and Mn in zone IV are reduced phases? Why not in other zones? Are there indications that Fe and Mn are present as Fe(II) and Mn(II)?

Line 402: ‘... decreased P retention was observed’. This reads as if the retention capacity had decreased (and maybe it has, due to much lower concentrations of Fe and Mn). But I assume you mean that the mass accumulation rate of P in the sediment has decreased?

Line 404: change to: “ were of autochthonous origin”. I do not understand why this is stated. HCl-P might be mainly P scavenged by biogenic calcite precipitation (autochthonous), but what kind of material is the refractory P? By which processes could this be produced?

Line 406: ‘Interestingly...’. My guess is that syphoning had an immediate effect on the concentration of TP in the lake. Monitoring data of the water column (unfortunately not shown in your paper) demonstrate a drop of TP during winter mixing from 125 mgP/m<sup>3</sup> (1975) to <50 mgP/m<sup>3</sup> (1987) (with no data in between). Therefore it is plausible that the P deposition rate decreased steeply.

Line 407: ‘... the lake in zone IV had higher eutrophic levels... (than in zone III)’. What parameters do you use to characterize trophic state? Certainly not TP, because TP concentrations have decreased ‘by a factor of 5-6 since 1978’ (line 400).

Line 414: in this context: As TP concentrations have decreased due to syphoning – why should ‘the enhanced retention of Ref-P be derived from increased algal refractory organic matter’? I assume that if you calculate the deposition rate of Ref-P (multiplication

with MAR) you would see that it has not changed significantly in recent years – (maybe indicating that it is of allochthonous origin?). In addition, an increasing concentration of any solid organic component towards the sediment surface (younger sediment) may be partly due to still ongoing metabolic processes and thus does not per se indicate an increasing sedimentation rate during more recent years.

Line 417-423: First, the authors do not state any quantitative information on observed water quality parameters. Second, I would speculate that the lake's trophic state did not respond to the hypolimnetic withdrawal because before syphoning P, Fe(II) and Mn(II) released from the sediment accumulated transiently only in the hypolimnion and re-precipitated when Fe(II) and Mn(II) came into contact with O<sub>2</sub> without affecting the P load to the trophogenic layer and, hence, primary production. After hypolimnetic withdrawal went into operation, the released P, Fe(II) and Mn(II) are exported, thus, do no longer precipitate and consequently the sediment depletes in P. TP concentrations after winter mixing decreased in subsequent years from 125 mgP/m<sup>3</sup> to ~25 mgP/m<sup>3</sup>, i.e., the lake was still fully productive. As less Fe and Mn is available to bind P in the sediment since the onset of deep water syphoning, the majority of P ending up in the sediment was scavenged by biogenic calcite precipitation. Briefly, the trophic state of Lake Burgäschi with its high flushing rate (0.7 yr<sup>-1</sup>) is not strongly affected by the hypolimnetic withdrawal, because in this relatively deep lake, primary production depends primarily on the lake's external but hardly on its internal P-loading. In brief, phytoplankton in the epilimnion “does not care” about hypolimnetic P concentrations.

Line 421: Nitrogen limitation: According to the chemical monitoring data of the water column in the years 2000-2010 concentrations of nitrate were always 0.6 – 3 mgN/L or higher in the trophic zone in September. This excludes nitrogen limitation.

Line 428: This remark insinuates that before 1977 the hypolimnion was partly oxic. This contradicts the observation of laminated Fe/Mn patterns in the sediment even in zone I. In line 347 you interpret Fe/Mn patterns in zone II “as the results of stable anoxic hypolimnetic waters”.

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Line 431: It is obviously too general and imprecise that ‘the dominant factor controlling ... P in the sediments ... was found to be autochthonous Fe and Mn content in anoxic sediments ...’ because on line 437 it is stated that ‘... Ca-P fraction predominated in surface sediments after 1977’.

Line 432: Why do you claim that the benthic Fe and Mn was of autochthonous origin? What exactly do you mean?

Line 436-439: Why do you think that hypolimnetic water syphoning can lower the lake’s external P loading? This conclusion is not supported by any data.

Line 440: Already discussed above. This is a matter of the algae-available P-load and how much of it can be removed from the lake. Due to the short water residence time, a large fraction of the algae-available P effective in primary production enters the epilimnion of the lake during the stratified period and is not affected by the deep water syphoning. Since the load from the catchment was not at all affected by the installation of the syphon, there is no reason to assume that the P load available for production (i.e. the TP present in the trophic zone after winter turnover plus the load of algae-available P flushed into the lake during the productive period) has significantly decreased to affect primary production. Nitrogen limitation can be excluded, and the effect of global warming might affect the duration of the stratification time but certainly does not significantly increase productivity in Burgäschisee.

Line 443-444: I fully agree here!

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