Manuscript ID bg-2019-389 titled “**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**”.

We would like to thank the two reviewers for their thoughtful comments and constructive suggestions, which help to improve the quality of this manuscript. Our response to each reviewer follows.

RESPONSE TO COMMENTS of Anonymous Referee #1

General response: We would like to express how much we appreciate the comments and feedbacks provided by Anonymous Referee #1. We have addressed the comments point by point below. As we agree with the comments and have made additional calculations (e.g. fluxes), we are confident that we can address the comments adequately in a revised version of the manuscript.

General comments R1: 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.

General Response: Reviewer 1 (R1) raises several important questions that help significantly improve the manuscript (see specific comments and responses below). In a revised version, we implement the following major modifications and emphasize the issues raised by R1:

- We will frame our Introduction (and specify/reframe the motivation for your research) more towards the effects in the sediments found after hypolimnetic syphoning. We find it noteworthy (thanks to the suggestion by R1) that the sediments actually do show a positive result (and the one that has been predicted) after the remediation measures, whereas the effects found in the water body (e.g. productivity) remain mixed (BVE/GSA 2007: "*30 Jahre Tiefenwasserableitung: Wie geht es dem Burgäschisee heute*"). We will also include a discussion about similarities and differences with other lakes where hypolimnetic syphoning has been installed, limnological parameters were monitored in subsequent years (e.g. Lake Mauen, Gächter, 1976, a lake which is larger but shallower). This places our study in a larger context.
- We place more emphasis on within-lake processes and the effect of water withdrawal (with regard to Fe and Mn removal from the lake system) to interpret our data from the sediments.
- From comments by R1 and literature for Lake Mauen (Switzerland) and lake Burgäschi (our study, Switzerland) it appears that, in Lake Burgäschi, the most obvious improvement of lake remediation (here: syphoning) are actually found in the sediments (net P burial rates, P speciation and potential for the release of internal P loads) whereas relatively little effect is found in the lake itself. Confirming respective predictions (e.g. Gächter, 1976) with sediment data was precisely the reason and motivation for our study. In contrast to well-mixed shallow lakes, there are still very few studies available assessing P speciation

and P speciation net burial rates in deep, seasonally or permanently anoxic lakes. Our study is, therefore, important and to some extent unique as we can assess the long-term effects (> 40 years) of lake remediation in a system where also very good limnological monitoring data are available. Accordingly, we modified and shaped the scope of our study (Introduction) to make the new contribution better visible.

- Most of the ‘contradictions’ mentioned by R1 are due to imprecise language. Content-wise, we fully agree. We also point much better to the Supplementary Online Materials (for clarification).

Specific comments:

1. 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.

   Response: Thank you for pointing to the study by Gächter (1976) in Lake Mauen. In the revised Introduction (revised manuscript), we summarize the major results of this study (observations from the water body and inferences for the sediment P) for the points 1-4 (mentioned above). Yes, our data (long-term P speciation in sediments, the focus of our manuscript) fully support what has been predicted from limnological observations and mass balance calculations to occur in sediments (e.g. Gächter 1976). This is the most valuable contribution of our manuscript – again, we would like to point out that there are only a very few studies available from deep, seasonally or permanently anoxic eutrophic lakes documenting the long-term effect of hypolimnetic syphoning on P-species net burial rates in sediments (in contrast to studies of P-speciation in shallow holomictic lakes).

2. 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 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).

Response: We have added more interpretation regarding eutrophication and pigment preservation (Line 230-231 in the revised manuscript, Section 3.3). The sediments in Lake Burgäschi are mostly laminated and organic-rich (Van Raden, 2012), and fully anoxic. In principle, pigments preserve well under such conditions (Reuss, 2005). A recent study on early diagenesis of pigments in laminated anoxic sediments (Rydberg et al., currently under review with JOPL; the sediments are comparable to those of L Burgäschi) suggests (i) that pigment diagenesis is restricted to the topmost sediment (few years) and (ii) that ‘unspecific’ hyperspectral techniques (similar to our technique) are most robust (much better than e.g. HPLC) to assess ‘original’ pigment concentrations, because all the pigment degradation products are also summarized. Similarly, our ‘green pigment’ index ($RABD_{590-765}$) includes both chlorophylls and all diagenetic products (sum of all), and we do not look at the pigment ratios, ‘freshness’ or potential for degradation of chlorophylls (cf. Schubert et al., 2005) or Chlorophyll Preservation Index CPI.

We add more references (using spectral indices as a proxy for paleo-productivity, e.g. from Lake Ponte Tresa, Southern Switzerland); we are confident that our pigment index does reflect paleoproductivity in Lake Burgäschi (qualitatively, as we use it, not overstating).

Reuss, N., 2005. Sediment pigments as biomarkers of environmental change. DMU report.

3. 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)?

Response: Fraction 5 (F5) represents the refractory organic P. TP is the sum of the five fractions (F1-F5). We added the protocol in Fig. S3 (Supplementary Online Materials; SOM). We clarify this in the text, see also Fig. S3.

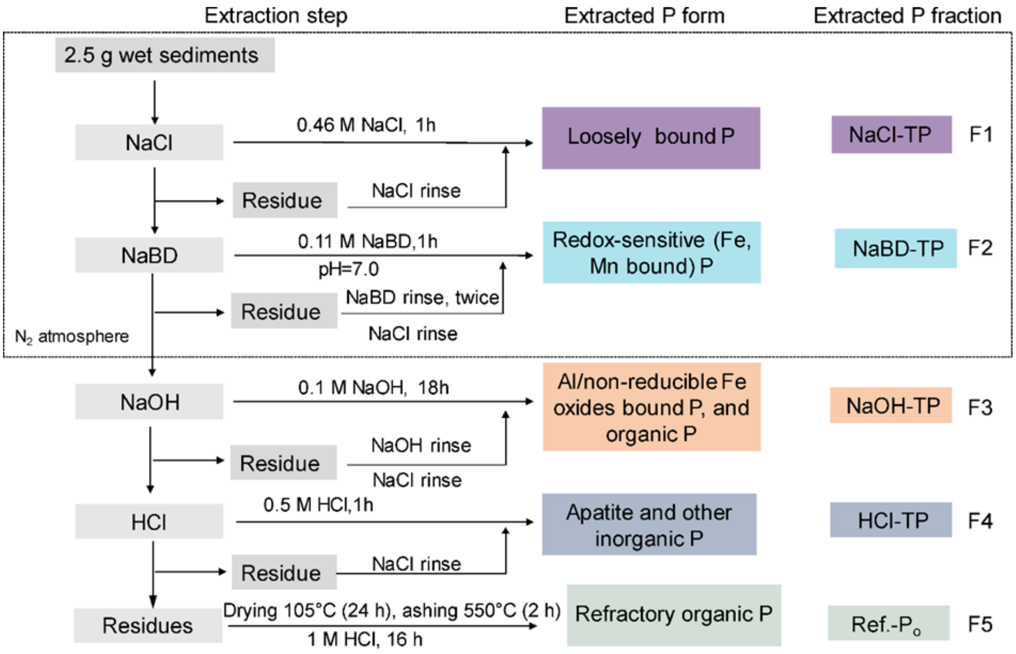


Figure S3

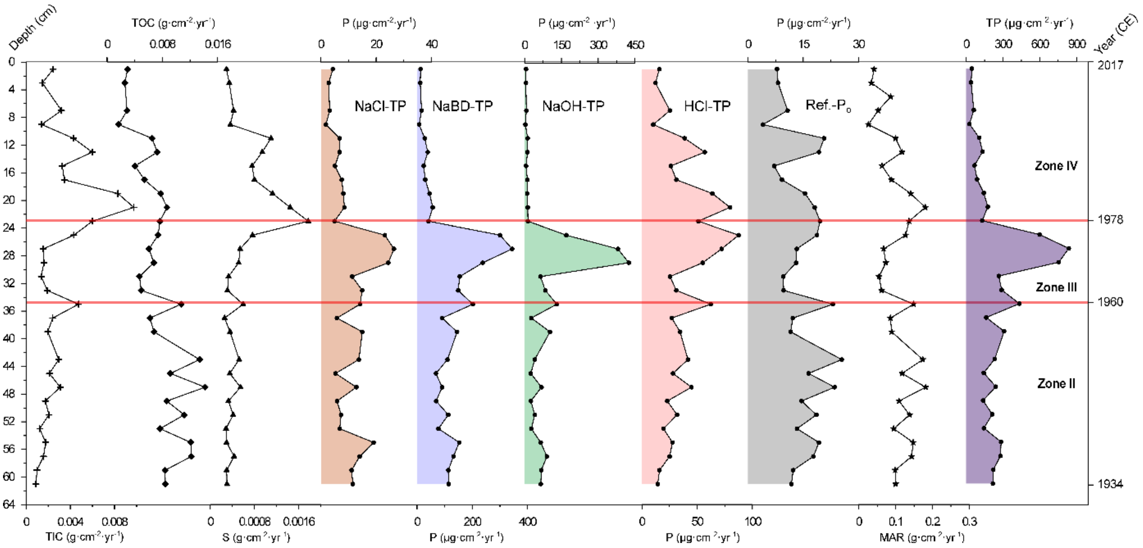
4. Line 274: “Afterwards” is confusing, because sediment age decreases downwards. Suggestion: Replace “Afterwards” by “then, with decreasing age, they increase…. ”

Response: Done, modified.

5. 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.

Response: Thank you for this suggestion. Yes, we calculated and added the fluxes (i.e. Net burial rates; $\mu g \cdot cm^{-2} \cdot yr^{-1}$) of all P fractions, TIC, TOC TP and sediment mass accumulation rates (MAR) of Core Burg17-C in Fig. S9

(Supplementary online materials). As MARs (calculated from the CRS ^{210}Pb model) are quite constant, results do not change much except for the decreases of HCl-TP flux and Ref.-P$_o$ flux after 1978. This is interesting (added in the text).



New Figure S11

6. 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.

Response: See our comment above. Yes, this is a very critical issue which we are aware of. Given existing literature, the sediment taphonomy of L Burgäschi is ideal for pigment preservation. Our record does not show a pronounced ‘tailing’ in the top 1-3 cm of the sediment which would indicate early diagenetic processes. As mentioned above, the spectral index of “green-pigments” includes all degradation products of chlorophylls. Pigments and their diagenetic products have shown to be a useful reliable proxy for past eutrophication if taphonomic conditions are suitable. We add more references, including *Leavitt, P. R and Hodgson DA.: Sedimentary pigments. In: Smol JP, Birks HJB, Last WM (eds) Tracking environmental change using lake sediments, vol 3. Terrestrial, Algal, and Siliceous Indicators. Kluwer, Dordrecht, pp 295–325, 2002.*

7. Line 292: Delete ‘with each other’.

   Response: The correction has been made.

8. Lines 295 to 297: See comment to line 291.

   Response: See the responses to Comments #1 and #6.

9. 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.

   Response: It is the CRS-2 model which is valid and places AD 1943 at ca 48 cm sediment depth. At this depth (above and below) none of the sediment proxies or elemental composition does show an anomaly or change. This is interesting indeed. As suggested, more discussion about the effects of lake-water level lowering in 1943 has been added in Line 410-412.

10. 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).

    Response: As suggested, we have rewritten this part and more explanation has been given in Line 416 (revised marked-upmanuscript).
    We have added a Figure with the fluxes for those proxies where this is possible (see above Fig. S9). Calculating fluxes is not possible for all elements measured with XRF on wet sediment (unit cps) because of changes on porosity, water contents among others. Again, MAR and sediment

componentry are relatively homogenous throughout the sediment core; thus, we do not expect major differences between concentrations (% or cps) and Flux that would change the interpretation.

11. 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?).

Response: Yes, bottom water anoxia in Lake Burgäschi was common during the stratified season, as the lake is quite deep (max. 31m) compared with its small surface 0.21 km^2. We refer to van Raden (2012) who described the redox varves in Lake Burgäschi as a result of seasonal changes in redox conditions. Redox varves were present in this lake since prehistoric times. Added in the text.

12. 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 O2 consumption in the hypolimnion, which reaches a maximum rate of 1.1 g O2 m-2d-1 for productive lakes. Moreover, the O2 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.

Response: Yes, this is correct and was not clear from the text (wording). We do not draw inferences from the Fe/Mn pattern on PP. The observation of increased PP comes from the pigment data. We precisely meant that oxygenation and the presence of Mn in redox varves is naturally very sensitive to increasing PP. We rephrased and added information from Section 5.1 to discuss lake primary productivity in Zone III (Line 447).

13. Line 362: Replace “no” by “absent”.

Response: Done, modified.

14. 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 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.

Response: Thank you for this important notion. Yes, as suggested, we calculated the annual net burial rate of all P fractions and TP in sediments, as shown in Fig. S9 (SOM) or see the Figure above in responses to Comments #5. In fact, this shows that Ca-TP fluxes slightly decrease between ca 1980 and the present. During this time, the Ca-TP fraction evolves to the dominant sedimentary P-fraction (relative to the other P fractions). We also refer to Gächter (1976) who pointed to the relationship between the Fe-P and the Fe-S cycle and discuss the other effects of deep water syphoning (removal of Fe and Mn ions). More interpretation and discussion about the effects of hypolimnetic water withdrawal on annual deposition rates of P fractions since 1977 have been added in Section 5.3.

15. Line 382ff: Replace Â´ncovingÂ˙z by Â´ncovering” 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.

    Response: Yes, we agree that after 1977, P retention in sediments is mainly due to biogenic calcite formation. This is different from TP in the entire sediment profile which has – prior to hypolimnetic syphoning - a close relationship with autochthonous Fe (Fe/Ti), Mn and hypolimnetic oxygenation (proxy Fe/Mn ratios), as suggested by the results of the RDA analysis. We rephrase the second and third paragraphs in Sect. 5.3, and distinguish between Zone IV and the rest (Line 512-514).

16. 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.

    Response: Yes, we agree that all Fe and Mn in sediments originate from the catchments, but in different forms (lithogenic or dissolved in the water). The Fe/Ti ratio represents in fact both, the allochthonous or autochthonous (endogenic and authigenic) Fe sources: assuming that Fe/Ti in lithogenic material is constant, excess Fe/Ti represents the redox-sensitive autochthonous fraction which is relevant for P precipitation (Zarczynski et al., 2019). This is clarified in the revised text.

    Żarczyński, M., Wacnik, A. and Tylmann, W.: Tracing lake mixing and oxygenation regime using the Fe/Mn ratio 648 in varved sediments: 2000 year-long record of human-induced changes from Lake Zabinskie (NE Poland), Sci.Total Environ., 657, 585-596, 2019.

17. 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?

Response: a) We acknowledge that this is important but, unfortunately, we do not have information about the binding form. We also expect diagenetic effects, maybe even bacterially mediated. b) NaOH-P includes Al/Fe oxyhydroxides bound P which might partly contain Fe (II)-P but we do not have geochemical indicators to separate Fe (II) from Fe (III).

18. 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.).

Response: Yes, this was not clear, we meant seasonal anoxia. We changed the sentence into "……better seasonal oxygenation than in Zone II and IV (see Sect. 5.2)". This is based on the presence of redox varves in Zone III.

19. Line 393: contradiction: 'Mn and Fe oxyhydroxides' are not 'reduced P-bearing solid phases'.

Response: Yes, this was misleading. We have changed it into "Mn and Fe minerals".

20. Line 394: What are 'more anoxic conditions'? Conditions are either oxic or anoxic.

Response: We remove "more".

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

Response: Yes, see our comments above. We have considered and added the effects of the hypolimnetic syphoning restoration also in this context.

22. 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)?

Response: We apologize for the confusion**.** We did not mean that "Fe and Mn in zone IV are reduced phases". We have replaced "reduced" by "decreased" to clarify that the preservation of Fe and Mn in sediments of Zone IV declined.

23. 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?

Response: yes, this was meant. We have changed the sentence to be more clear (Line 587-588).

24. 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?

Response: We have added more context: "…as indicated by absent positive correlations between the two fractions and detrital elements such as Ti, K and Al (Fig. 7)" in Line 594-595 to clarify the statement.
Refractory P comes mostly from ashing (550°C) of organic matter and, potentially in traces, also from fluorapatite in molasses bedrock of Lake Burgäschi.

25. 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/m3 (1975) to <50 mgP/m3 (1987) (with no data in between). Therefore it is plausible that the P deposition rate decreased steeply.

Response: We have rewritten this part and discussed the effect of hypolimnetic withdrawal on Ca-P annual deposition rates. We also have shown hypolimnetic TP monitoring data from 1977 to 2009 in the synthesis figure (i.e. Fig. S11) showing the rapid decrease as the result of hypolimnetic withdrawal.

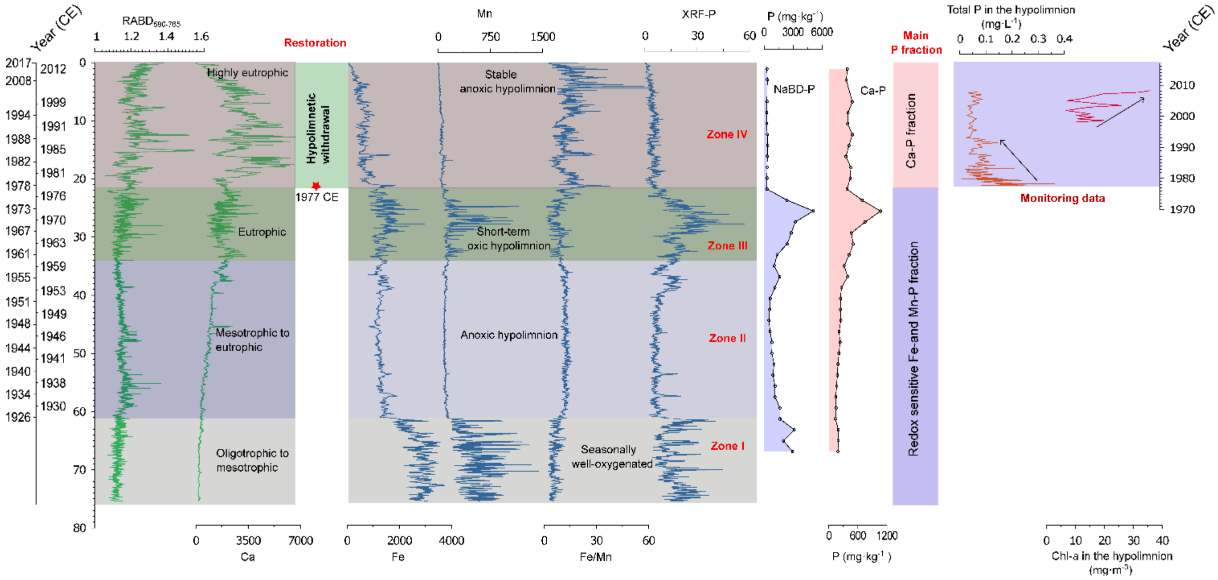


Figure S11

26. 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).

Response: "Higher eutrophic levels in Zone IV" was inferred from the interpretation of "green-pigments" index data, and also from the previous studies (see the last paragraph of Section 5.1). We clarified this in the text.

27. 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.

Response: Yes, you are right, thank you for this comment. The flux rates revealed a generally weakly decreasing trend of Ref.-P_o fraction in recent decades (Figure S10; Supplementary online materials). This goes hand in hand with a decrease in TOC fluxes suggesting a negative trend in aquatic primary productivity. More discussion, as suggested, has been added in the second-last paragraph of Section 5.3.

28. 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 O2 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/m3 to _25 mgP/m3, 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-1) 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.

Response: Yes, limnological data is shown in Suppl. Fig. S11 as mentioned above. Thank you for this comment, which is a very good point for the interpretation, and an important point for discussion in contrast to Lake Mauen (Gächter, 1976) which is larger and shallower. We have added more context and discussion in Line 680-683.

29. 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.

    Response: Agreed. We have removed "nitrogen limitation" from the possible factors.

30. 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".

    Response: We have changed the text in the Conclusions. Although here we have to clarify that "Persistent anoxic conditions in the hypolimnion after ~1977" is unrelated to the question "whether or not, before 1977, the hypolimnion was partly oxic" (which was seasonally the case).

31. 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'.

    Response: Yes, this is true, we need to differentiate between the zones. The correction has been made to clarify that "only before 1977, P retention in sediments was mainly controlled by autochthonous Fe and Mn content in anoxic sediments". After 1977, hypolimnetic withdrawal restoration played a role in P retention in sediments.

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

    Response: Autochthonous origin of Fe and Mn means that Fe and Mn preserved in sediments is mainly controlled by redox and diagenetic processes (i.e. in-lake processes) rather than by clastic inputs. That is why we call it "autochthonous". The sentence is clarified.

33. 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.

    Response: Yes, this is not what we meant. We have corrected the sentence and removed the "external P loading".

34. 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.

    Response: Agreed, absolutely. Maybe the argument was confusing, but we did not mean that syphoning would decrease external P loads. We fully agree. This is the reason why it is very important to assess sediment P (fluxes and speciation) in order to evaluate the effect of remediation (in this case hypolimnetic syphoning). We have added more context in the Conclusions to reinforce this implication; moreover and accordingly, we rephrased the

Research Questions and Motivation in the Introduction to clarify why it is important to look into sediments.

35. Line 443-444: I fully agree here!

RESPONSE TO COMMENTS of Anonymous Referee #2

General comments: Luyao Tu and co-authors present a _120 year-long sedimentary record from Lake Burgäschi on the Swiss plateau discussing variations in the bottom-water oxygenation state, the trophic state and potential phosphorous retention/release during these varying conditions. The data set of the study including phosphorous fractions, carbon, sulfur and nitrogen concentrations, XRF core scanning, and hyperspectral imaging is extensive. Yet, in my opinion it is partly overinterpreted and partly not clearly presented. What I am missing is a better linkage of the data with the development of agriculture and deforestation in the lake's catchment area and with the lake's restoration history. Interpretations on the trophic state and the reconstruction of hypolimnetic oxygenation regimes are given in the discussion section but with only weak links to the human influences that are potentially responsible for these variations. However, since the study cannot contribute much to the already known chemical mechanisms of phosphorous retention/release in lake sediments, it seems important that the findings be interpreted with regard to these same human influences.

Overall, my impression after having read the manuscript was that there is a lot of data,
a lot of statistical analysis but the promise from the abstract that I would learn how hypolimnetic anoxia influence lake recovery from eutrophication was not accessible to
me. It may be that it is included in the manuscript but then in a form that is difficult to access for the readership. Accordingly, the manuscript should be revised. More focus should be put on the interpretation of the data in a larger context. But the data should

also not be overinterpreted as in section 5.3. Currently, the technical and statistical side dominates. I recommend for instance the design of scenarios in the form of conceptual models (sketches) demonstrating the processes that were dominating the lake during Zones I to IV. For the readership, this would make the outcome of this study much more attractive and accessible.

Response: We thank the Anonymous Referee #2 for the valuable and thoughtful comments which add substance to our manuscript, balance the interpretation (more cautious) and improve clarity and readability. Some of the are in line with Reviewer 1. Accordingly, we rephrased (clarified) the primary aims of our study, namely to assess and evaluate the lake remediation measurements (here syphoning of hypolimnetic water) from the viewpoint of sediment profiles, i.e. with data on P fractions, P burial rates and risks for internal P release in and from lake sediments. In most cases remediation is assessed with limnological data. Here we can show that the largest effect of remediation is actually observed in the sediment P pool and its fractions; effects on lake productivity are marginal. The view from lake sediments is critical. Indeed, we confirm with sediment data what has been predicted from limnological data. But in contrast to shallow polymictic lakes, there are only a few studies showing sedimentary P fractions and pools for deep seasonally or permanently anoxic lakes. But we agree: our sediment data need much better discussion in the context of the general eutrophication history and hypolimnetic water withdrawal (with processes). Yes, we added a sketch figure (Fig. 8) with the conceptual model for the four stages discussed in the text.

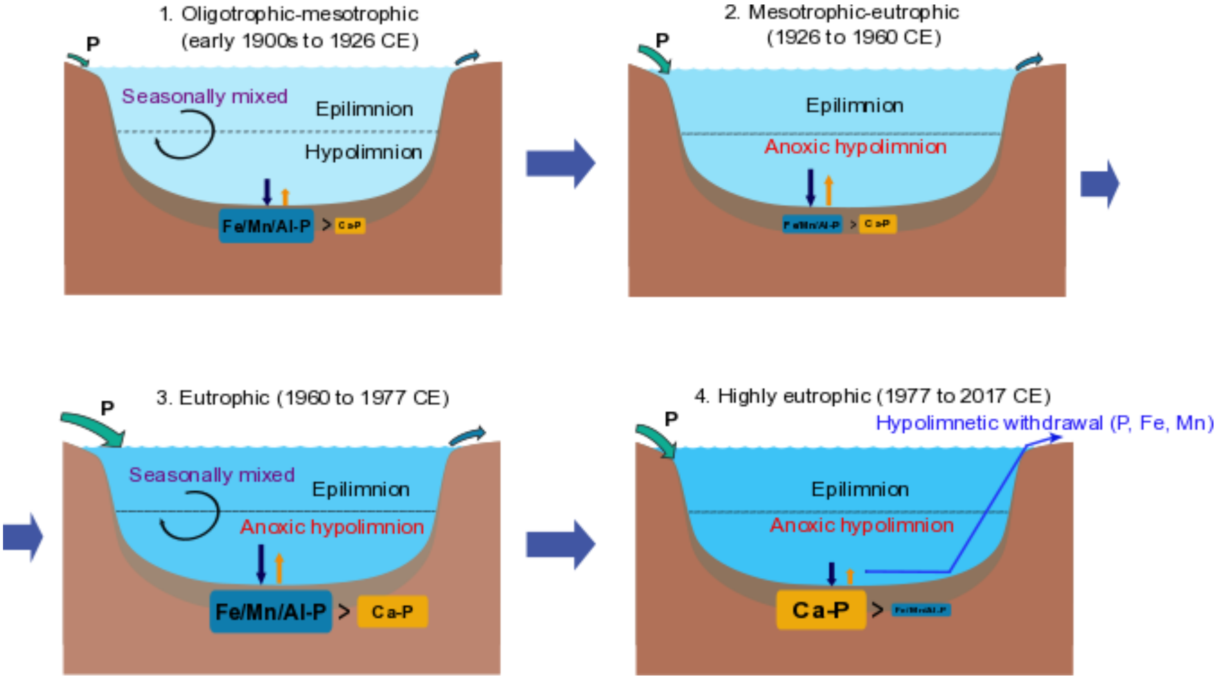


Figure 8

Specific remarks:

1. Line 44: ‘oxygen levels’ (not only oxygen) More details should be given in the Introduction on the principle and aim of the phosphorous analysis. Also, one sentence more on the technique of the P analysis should be added to ‘3.4 Phosphorus fractionation scheme and bulk element analyses’ where the authors simply refer to Tu et al. (2019) for the details (line 171). This shortness on the P analysis is questionable given the importance it has for the study. At one point or the other (Introduction or Material and methods) more detail should thus be provided.

   Response: The correction has been made as suggested. Yes, the Introduction (specifically the Aim and Motivation for our study; the significance of sedimentary P-fraction retention; the research gaps) is rephrased accordingly. We added more text to the P extraction scheme and added a new Figure with the extraction scheme in the Fig. S3 in Supplementary online materials (SOM).

]

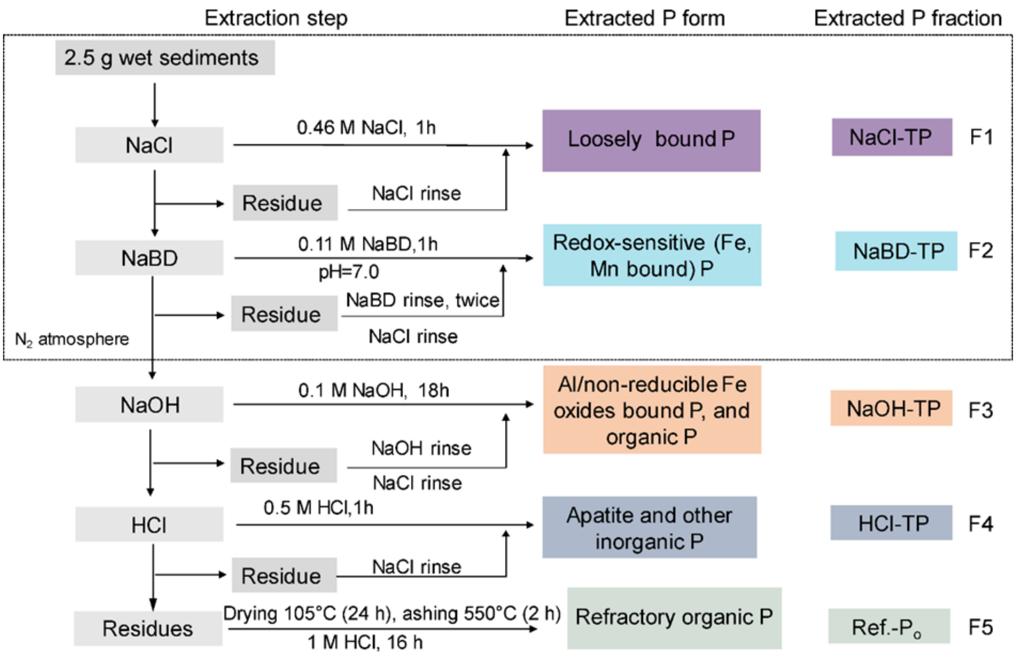


Figure S3

2. Line 90: A lake has always just one single outflow.

   Response: Yes, Lake Burgäschi only has one outflow (Line 138).

3. Line 91-92: I guess it should read ‘the most important lowering’.

   Response: We have changed it into “the most recent lowering”.

4. Lines 112, 113: Referencing to sections that come later in the manuscript is usually not accepted (to be checked for Biogeosciences).
   Response: As suggested, the correction has been made.

5. 3.2 Chronology: Great detail on the activity analysis of 137Cs and 210Pb. Might not be necessary, but actually I welcome the point that it is once presented in a manuscript.

   Response: Thank you. Yes, we decide to leave it as is. A proper presentation of the age-depth model is fundamental (and often not made).

6. Line 152: ‘The core surface…..’

Response: Done, corrected.

7. Line 156: Add the appropriate elements to the description for the 10 kV and the 30 kV run, respectively.

   Response: As suggested, the correction has been made (Line 217-218).

8. Line 187: Provide at least a keyword on the method and not only the naked reference. As a reader I would like to know at least in which direction it goes before deciding if I want to search for the reference.

   Response: More description about the method has been added in Line 239 (revised manuscript). Also, the extraction scheme is added in Fig. S3 of SOM.

9. Line 304: This general increase in sedimentary green pigments I cannot see.

   Response: The slight increase in “green-pigment” index can be seen more clearly from Figure 4d.

10. Line 305: ‘green-pigment concentrations’

    Response: Done, corrected.

11. Section 5.3: This section is rather a mix of already presented interpretations on the state of the lake and interpretations that are speculative and are lacking the necessary data foundation (not given by the results from this study).

    Response: We have re-organized and re-written this section and make the interpretation from our results more logical and clear to follow, meanwhile with support of limnological monitoring data and previous studies.

12. Line 372: ‘Fe contents control’

Response: Done, corrected.

13. Lines 438-442: Here, finally a clear statement linking the data with lake restoration, agricultural influences etc. Points like this should be more elaborated during the Discussion section and not only brought forward (a bit out of nowhere) in the Conclusions.

    Response: We have added more context in Section 5.1 to explain how the agricultural activities can influence P loads into the lake and lake primary production (Line 410-412). This is a valuable additional comment to Reviewer 1.

14. Figure 3 with the lithological interpretations cannot come before the presentation of the XRF data in Figure 4 as you need the XRF data to define the lithologies.

    Response: As suggested, we have changed the order of Figure 3 and 4.

15. Figure 4: Too many elements shown. This is a common issue with XRF data. Mg should be deleted, this is noise, Mg is too light to be measured with an Avaatech scanner. Either Al or K is sufficient; I recommend K as it is heavier and therefore presents the more robust result. Ti is sufficient here (delete Rb). You could show Al and Rb in the supplementary material if you wish.

    Response: Yes, we agree. We have removed the XRF elements Al, Rb, Si, Mg and placed them into the new Fig. S6 (SOM).

16. Figure 6: Can be added to Figure 5. Might even be more illustrative to have all the P plots together in one graph.

    Response: Yes, we understand the point. But in fact, the two figures illustrate something different: Figure 5 (curve plot) displays the time-series changes of P fractions and LOI data from Zone I to IV. In contrast, Figure 6 (stacked bar plot) mainly aims to show the average proportions of the five P fractions in the sediments. We prefer to leave them as two Figures.

17. Figure 7: I do not understand how the colored points of the individual cluster zones are added to this graph. Please explain in the figure caption.

    Response: We clarify the source in the caption of Figure 7 (Line 1097).

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

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Abstract. Hypolimnetic anoxia in eutrophic lakes can delay lake recovery to lower trophic states via the release of sediment phosphorus (P) to surface waters on short time scales. However, the long-term effects of hypolimnetic redox conditions and eutrophication on sedimentary P-fraction retention in deep lakes are not clear yet. Hypolimnetic withdrawal of P-rich water is predicted to reduce sedimentary P and seasonal P recycling from the lake hypolimnion. Nevertheless, there is a lack of evidence from well-dated sediment cores, in particular, from deep lakes, about the long-term impact of hypolimnetic withdrawal on sedimentary P retention. In this study, long-term sedimentary P-fraction data since the early 1900s from Lake Burgäschi provides information on the potential availability and retention of sediment-P under the influences of increasing lake primary productivity (sedimentary green-pigments proxy), variable hypolimnion oxygenation regimes (Fe/Mn ratio proxy), and hypolimnetic withdrawal restoration since 1977. Results show that, before the operation of hypolimnetic withdrawal (during the early 1900s to 1977), redox-sensitive Fe/Mn-P fraction comprised ~50% of total P in the sediment profile. Meanwhile, long-term retention of total P and labile P-fractions in sediments was predominantly affected by past hypolimnetic redox conditions, and P retention increased in sedimentary Fe- and Mn enriched layers when the hypolimnetic had better seasonally oxic conditions. However, from 1977-2017, eutrophication-induced persistent anoxic conditions in the hypolimnion and hypolimnetic withdrawal both contributed to considerably decreased retention and net burial rates of total P and labile P fractions in surface sediments. By contrast, refractory Ca-P fraction retention was primarily related to lake primary production. Due to the lake restoration since 1977, Ca-P fraction became the primary P fraction in sediments (representing ~39% of total P), indicating a lower P bioavailability of surface sediments. Our study implies that in seasonally-stratified eutrophic deep lakes (like Lake Burgäschi), hypolimnetic withdrawal can effectively reduce P retention in sediments and potentials of sediment-P release (internal P loads). However, more than 40 years of hypolimnetic syphoning have not improved the lake trophic state or decreased lake productivity. The findings of this study are relevant regarding management of deep eutrophic lakes with mixing regimes typical for temperate zones.

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Keywords: Phosphorus fractions, eutrophication, hypolimnetic anoxia, hypolimnetic withdrawal, deep lakes

1 Introduction

Phosphorus (P) eutrophication in freshwater lakes is a global problem and has been a matter of concern to the public for several decades. In lakes where the external P loading has been reduced, internal P loading (sediment-P release to surface waters) is widely recognized as the key factor affecting lake trophic status and delaying lake recovery from eutrophication (Burley et al., 2001; Trolle et al., 2010). Considerable work has been done on sediment-P speciation to evaluate sediment-P release potentials and implications for lake restoration management (Gonsiorczyk et al., 1998; Ribeiro et al., 2008).

The paradigm that oxygen levels control the sediment-P release via reductive dissolution of Fe-P fraction in surface sediments has been accepted as the classical model for a long time (Einsele, 1936, 1938; Moosmann et al., 2006). Under anoxic conditions, P bound to redox-sensitive Fe and Al/Fe (oxyhydr)oxides can be potentially released from surface sediments into lake water (Burley et al., 2001), which was supported by numerous short-term (days or seasonal) laboratory or in-situ studies (Chen et al., 2018). Based on this paradigm, it was assumed that an oxic sediment–water interface might limit the release of Fe-P from sediments and, therefore, improve P retention in lake sediments. However, the restoration measures with artificial hypolimnetic oxygenation/aeration applied in eutrophic lakes proved to have only short-lasting effects but no direct effects on internal P loading and redox-dependent sediment-P retention on longer terms (Gächter, 1987; Gächter and Wehrli, 1998; Moosmann et al., 2006; Hupfer and Lewandowski, 2008). Gächter and Müller (2003) and Moosmann et al. (2006) further argued that, on multi-decadal or longer time scales, P retention in lake sediments might eventually primarily depend on the P-binding capacity of anoxic sediments and sediment composition (e.g. Fe, Mn, Al, and Ca contents). Nevertheless, until now, there is a lack of evidence from well-dated sediment cores, and there is still a need to know which processes may have a dominant influence on sediment P-fraction retention on longer time scales (e.g., decades or more). This information is crucial for predicting and, ultimately, managing sediment-P release, especially in deep lakes, because hypolimnetic anoxia in deep lakes can lead to large loads of sediment-P release. In contrast to the well-established studies about sediment-P speciation in shallow polymictic lakes (e.g. Kaiserli et al., 2001; Søndergaard et al., 2001; Cavalcante et al., 2008), there are only a few studies available from seasonally-stratified deep lakes. Furthermore, eutrophication has been demonstrated to affect sediment-P release via controlling hypolimnetic anoxia and lake mixing regime in seasonally stratified deep lakes (Tu et al., 2019). It is not yet fully understood whether and how lake trophic levels and hypolimnetic anoxia can influence the long-term behavior of sedimentary P-fraction retention in deep lakes.

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The restoration technique of hypolimnetic withdrawal has been frequently applied in seasonally stratified lakes in Europe (Kucklentz and Hamm, 1988; Nürnberg, 2007), whereby P-enriched water from the hypolimnion is discharged directly into the lake outflow. This restoration technique has been shown to efficiently reduce P concentrations in lake waters (Nürnberg, 2007). Hypolimnetic withdrawal was also expected to reduce P retention in sediments and seasonal P recycling from the lake hypolimnion to the upper waters, for example, in Lake Mauen, a shallow, eutrophic lake (maximum depth 6.8 m; Gächter, 1976). However, there is lack of empirical evidence from sedimentary P-fraction data, which provides valuable information on possible sediment-P release

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characteristics and potentials of internal P loadings. Furthermore, for deep lakes, the long-term influence of this restoration on sedimentary P release potentials is unclear.

The objectives of this study were to (1) explore the main factors controlling long-term changes of P-fraction retention in sediments of deep lakes, (2) investigate how sediment P-fraction retention responds to changes in lake eutrophication and hypolimnetic anoxia of the past prior to anthropogenic eutrophication, (3) examine the long-term effects of lake hypolimnetic withdrawal restoration on sedimentary P-fraction retention in seasonally-stratified deep lakes, and (4) evaluate with sediment-P data the predictions from Gächter (1976) that hypolimnetic withdrawal should result in reduced total P contents in sediments and sediment-P release to lake water. To achieve these objectives, we investigated short sediment cores from Lake Burgäschi, a deep and eutrophic lake on the Swiss Plateau. Sedimentary green-pigments (chlorophylls and diagenetic products) inferred from hyperspectral imaging (HSI) scanning and XRF-inferred Fe/Mn ratios primarily reflect lake trophic state evolution (aquatic primary productivity) and hypolimnetic oxygenation, respectively. A sequential P-extraction with five P fractions was performed to uncover P fractionation in sediment profiles. We combined all data to identify the dominant factors responsible for temporal changes in P-fraction retention. Changes in P-fraction records for the periods before and during the restoration were also investigated.

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Lake Burgäschi is an excellent study site because there were substantial changes in lake trophic levels and possibly lake-mixing regimes since the last century (Guthruf et al., 1999; Van Raden, 2012), and exceptionally long historical and limnological survey data are available for most of the last 50 years. Hypolimnetic withdrawal restoration has operated in the lake since 1977.

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2 Study site

Lake Burgäschi (47°10′8.5″N, 7°40′5.9″E) is a small lake located on the Swiss Plateau (Fig. 1a). It has a very restricted catchment (3.2 km^2). The catchment area geologically belongs to the Molasse Basin, and mostly consists of carbonate-rich sandstones and mudstones (Schmid et al., 2004). The kettle hole lake was formed after the retreat of the Rhone glacier (ca. 19 k yr. BP; Rey et al., 2017). Currently the maximum water depth is ~31 m, which is quite deep in contrast to the small surface area of 0.21 km^2 (Guthruf et al., 1999). The mean retention time of the lake water is ~1.4 year (Nürnberg, 1987). The lake has several small inflows in the southwest (Rey et al., 2017) and one outflow in the north (Fig. 1c).

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Since the 19th century, the lake's water level was lowered several times to create agricultural lands, with the most recent lowering (up to 2 m) during 1943-1945 (Guthruf et al., 1999). Agricultural area currently covers ~55% of the lake catchment, followed by ~29% area of forests. The lake region experiences a warm humid continental climate (Dfb; Köppen-Geiger classification). The mean annual temperature is 9 °C and the warmest month is July (mean temperature 19 °C).

Lake Burgäschi has been highly productive (eutrophic to highly eutrophic state) since the 1970s with high algal-biomass production and anoxic conditions in the hypolimnion (Guthruf et al., 1999, 2013). The eutrophication in Lake Burgäschi has been linked to increased agricultural P inputs via drainage into the lake in the second half of the 20th century (Guthruf et al., 1999). To mitigate the eutrophication, hypolimnetic withdrawal restoration has been applied in Lake Burgäschi since 1977, and the lake water has been monitored twice a year for more than 30 years for various parameters, such as pH, oxygen content, phosphorus concentrations, phytoplankton biomass, etc. Despite a sharp decline in hypolimnetic phosphorus concentrations due to the restoration, a high production of algae biomass continues today (GSA, 2007). Additionally, hypolimnetic oxygenation conditions and the lake trophic state have been stabilized but not fundamentally improved (GBL, 1995; Guthruf et al., 2013).

3 Materials and methods

3.1 Core collection and sampling

In September 2017, two 75-cm-long sediment cores (Burg17-B and Burg17-C) were retrieved from the deepest point of Lake Burgäschi (water depth ~31 m) (47°10'8.6"N, 07°40'5.3"E; coring site in Fig. 1c) using a UWITEC gravity corer. After the collection, the cores were stored in a dark cold room (~4 °C). After opening and splitting lengthwise, core-half A of Burg17-B was continuously subsampled at 2-cm resolution from 0 to 60 cm for ^{210}Pb and ^{137}Cs dating. The oxidized surface of core-half B (Burg17-B) was visually described (Schnurrenberger et al., 2003) before non-destructive XRF core and HSI scanning. After the opening, one-half of core Burg17-C was transferred immediately into a glove box with an anoxic atmosphere where it was continuously subsampled at 2-cm resolution from 0 to 72 cm. The fresh sediments from each sample slice were homogenized and used for sequential P extraction. Afterwards, the remaining sediment was freeze-dried and homogenized for bulk element analyses.

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3.2 Chronology

The chronology of the core Burg17-B is based on ^{210}Pb and ^{137}Cs activity profiles. The freeze-dried and homogeneous samples were stored dry and dark until analysis. The ^{210}Pb, ^{137}Cs and ^{226}Ra radiometric activities were measured by gamma spectrometry at the University of Bern Department of Chemistry and Biochemistry. 1.3-5.1 g of the freeze-dried samples were encapsulated into polystyrene petri dishes (68 mm O.D., 11 mm height; Semadeni, Ostermundigen, Switzerland) together with a polystyrene disk to fill in the headspace above the sample material, and the petri dishes were vacuum-sealed into a gas-tight aluminum foil for equilibration. ^{210}Pb (46.5 keV), ^{241}Am (59.5 keV), ^{226}Ra progenies ^{214}Pb and ^{214}Bi (295.2, 351.9 and 609.3 keV), as well as ^{137}Cs (661.7 keV) were measured using a Broad Energy Germanium (BEGe) detector (Canberra GmbH, Rüsselsheim, Germany). This system is composed of a high-purity germanium crystal of 50 cm^2 area and 30 mm thickness with a 0.6 mm thick carbon epoxy window, which shows high absolute full-energy peak efficiencies for close on-top geometries of >20% and ~5% for ^{210}Pb and ^{137}Cs, respectively. Low integrated background count rates of 0.20 s^{-1} (energy range of 30-1800 keV) were achieved by application of low-background materials, installation in third underground floor (~10 m of water-equivalent overburden), passive shielding (outside to inside: 10 cm low-background lead, 3 mm ancient lead with negligible ^{210}Pb content, 2 mm cadmium), flushing of the shield interior with nitrogen gas and an active anti-cosmic shield (plastic scintillator panels of totally 1 m^2 area mounted directly above the passive shielding). Supported ^{210}Pb in each sample was assumed to be in equilibrium with the in-situ ^{226}Ra (equilibration time 4 weeks). Unsupported ^{210}Pb activity was calculated by subtracting ^{226}Ra activity from total ^{210}Pb activity level-by-level. The correction for the total unsupported ^{210}Pb missing inventory followed Tylmann et al. (2016).

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The ^{210}Pb chronology of core Burg17-B was determined using the Constant Rate of Supply (CRS) model (Appleby, 2002), which accounts for variation in sediment accumulation rates. We tested two CRS models: CRS-1 model was unconstrained (i.e. without reference points from the ^{137}Cs activity). The CRS-2 model was constrained with the chronologic marker of peak fallout from nuclear weapons testing in 1963 (^{137}Cs and ^{241}Am). Both models were then tested and validated with independent time-markers at the onset of nuclear weapons testing in 1953/54 and the Chernobyl accident in 1986/87 (onset of ^{137}Cs and peak of ^{137}Cs and ^{241}Am, respectively).

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The two sediment cores (Burg 17-B and Burg 17-C) are visually very similar but show a length-offset due to coring compaction of approximately 2-6 cm (Fig. S1 in Supplementary data). The age-depth stratigraphy of Burg17-C core was inferred from the dated core Burg17-B by visual stratigraphic correlation from high-resolution core pictures.

3.3 Non-destructive geochemical methods

Non-destructive X-ray fluorescence (XRF) core scanning was done using an Avaatech XRF Core Scanner (Richter et al., 2006) for semi-quantitative element composition measurements at 0.5 mm resolution to capture relative elemental concentrations of the laminae. The core surface was smoothed and covered with a 4-µm-thick Ultralene foil prior to the analysis. Elements were measured using a Rhodium anode and a 25 µm Be window. The lighter elements (e.g. Al, Si, P etc.) were measured for 15 seconds count time at 10 kV with 1500 A, no filter; while the heavier elements (e.g. Mn, Fe, Br etc.) were exposed for 40 seconds at 30 kV with 2000 A, Pd-thin filter. Element intensities (semi-quantitative concentrations) of the selected elements (Mg, Si, Al, K, Ti, Rb, P, Fe, Mn, Ca) are expressed as count rates (counts per second, cps).

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Following the methodology in Butz et al. (2015), hyperspectral imaging (HSI) scanning was performed using a Specim Ltd. Single Core Scanner equipped with a visual to near infrared range (VNIR, 400–1000 nm) hyperspectral linescan camera (Specim PFD-CL-65-V10E). Parameters were set for a spatial resolution of ~70 µm/pixel and a spectral sampling of 1.57 nm (binning of 2). Spectral endmembers were determined using the "Spectral Hourglass Wizard" of the ENVI 5.5 software package (Exelisvis ENVI, Boulder, Colorado). The relative absorption band depth (RABD) index calculation was performed following the method in Schneider et al. (2018). However, based on the spectral end members (Fig. S2), we used the absorption feature between the wavelengths R590 and R765 (590-765 nm), i.e. $\text{RABD}_{590\text{-}765}$. Butz et al. (2017) and Schneider et al. (2018) revealed that this index is well calibrated to absolute green-pigments (chlorophyll *a* + pheophytin a) concentrations in sediments. The sediments in Lake Burgäschi are mostly laminated and organic-rich (Van Raden, 2012), which indicates that the sediments are anoxic, bioturbation is absent, and sedimentary pigments are well-preserved (Reuss et al., 2005). Therefore, in our study, the relative concentrations of green-pigments inferred from $\text{RABD}_{590\text{-}765}$ index values provide a semi-quantitative reconstruction of lake primary productivity (total algal abundance) at sub-annual resolution, and are suggested to reflect the trophic state evolution of Lake Burgäschi.

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3.4 Phosphorus fractionation scheme and bulk elements analyses

The P-fractionation extraction protocol (Fig. S3) principally follows the four-step extraction protocol in Tu et al., (2019). In addition, we added the last extraction step from Lukkari et al. (2007) to determine refractory organic P (F5). This P fraction (F5) is practically biologically unavailable and subject to permanent P burial. The first four fractions are NaCl-TP (F1: loosely bound P), NaBD-TP (F2: redox-sensitive Fe- and Mn-bound P), NaOH-TP (F3: Al- and Fe-bound P), and HCl-TP (F4: Ca-bound P) (Tu et al., 2019), whereby NaCl-TP, NaBD-TP and NaOH-TP fractions together as considered relatively labile P fractions because they may release P back to the water column under anoxic or high pH environments (Rydin, 2000). The HCl-TP and refractory organic P (Ref.-P_o) fractions are classified as relatively stable or refractory P fractions. Total P in sediments was obtained from the sum of the five P fractions. The P in extract samples was measured by inductively coupled plasma mass spectroscopy (7700× ICP-MS) (Agilent Technologies, Germany) after the dilution with nitric acid (HNO_3) to reach a final concentration of 1% v/v HNO_3.

Concentrations of total carbon (TC), total nitrogen (TN), and total sulfur (S) in sediment samples were determined using an Elementar vario EL Cube elemental analyzer. Total inorganic carbon (TIC) content was calculated by multiplying loss on ignition at 950 °C (LOI_{950}, following the method proposed by Heiri et al. (2001)) by 0.273, i.e. the ratio of the molecular weight of C and CO_2. Total organic carbon (TOC) content was calculated using the equation TOC =TC-TIC. Sediment dry bulk density and water content were determined using wet mass (g), dry mass (g) and wet volume (cm^3) following the method in Håkanson and Jansson (2002).

3.5 Data analyses

Multivariate statistical analyses were performed with R version 3.4.2 (R Development Core Team, 2017). Prior to data analyses, $RABD_{590-765}$ index values (resolution 70 µm) were aggregated to a spatial resolution of 0.5 mm (the spatial resolution of XRF data). Stratigraphically constrained incremental sum of squares clustering (CONISS; Grimm, 1987) was then performed on semi-quantitative proxies (i.e. $RADB_{590-765}$ index and XRF-element data) with R-package ''rioja'' (Juggins, 2017). The number of significant clusters was determined with a broken-stick test (Bennett, 1996). A principal components analysis (PCA) was performed on the centered and standardized data of semi-quantitative proxies, using the "Vegan" package (Oksanen et al., 2013). XRF-element and $RABD_{590-765}$ index values were averaged within the depth range of each sample taken from core Burg17-C for P fractions. In order to identify the primary factors influencing the variations in sedimentary P fractions, a redundancy analysis (RDA) was performed on the centered and standardized dataset of P fractions (response variables) and other sediment geochemical parameters (explanatory variables) with the "vegan" package. In the RDA computation, the correlation matrix option was selected and the scaling was conducted on a correlation biplot.

4 Results

4.1 ^{137}Cs and ^{210}Pb chronology

The two distinctive peaks of ^{137}Cs in sediment profiles are detected at 31 cm and 15 cm depths (Fig. 2b), corresponding to the 1963 and 1986 major fallout events, respectively (Appleby, 2002). Furthermore, ^{241}Am activity peaks at the same depths (Fig. 2b) confirm that the 1963 and 1986 ^{137}Cs peaks were due to atmospheric

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fallouts (Michel et al., 2001). The first traces of ^{137}Cs occur at 37 cm depth, indicating the first widely detectable fallout from atmospheric nuclear testing in 1953/1954 (Pennington et al., 1973).

The ^{210}Pb activity in core Burg17-B shows a relatively monotonic decrease down to a sediment depth of 17 cm. Further down, larger variations are found (Fig. 2a). The ^{210}Pb and ^{226}Ra activities do not reach equilibrium; unsupported ^{210}Pb activity in the oldest sample (59 cm) is still above the limit of detection (14.0±6.8 Bq·kg^{-1}). The observed cumulative inventory of unsupported ^{210}Pb is 2941 Bq·m^{-2}. We corrected this value (missing inventory correction; Tylmann et al., 2016) by applying an exponential equation using the lowermost values of cumulative dry mass and unsupported ^{210}Pb activity between 8 and 60 cm depths. As a result, a correction value of 125.2 Bq·m^{-2} (missing inventory) is added to the final total unsupported ^{210}Pb inventory (3066 Bq·m^{-2}).

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The CRS-2 model (constrained through 1963) shows a better agreement with the independent ^{137}Cs markers at 1953/54 and 1986/87 than the CRS-1 model (Fig. 2c). Therefore, CRS-2 model results were chosen for determining the age-depth profile and sediment mass accumulation rates (MAR) of core Burg17-B. The mean age at 59 cm sediment depth dates back to ~1930. The extrapolated mean age at 61 cm depth is ~1926 calculated using the mean sediment accumulation rate between 54-60 cm (2 yr·cm^{-1}).

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4.2 Sediment lithology, green-pigments (RABD$_{590-765}$ index) and XRF-element records

Four sediment facies (I to IV, Fig. 3 and 4a) are identified based on visual classification and the CONISS-analysis results of XRF-element intensities.

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In Zone I (75.4-61cm, pre ~1926), the sediments consist of visible thin brown-to-reddish laminae (Mn- and Fe rich). Green-pigment concentrations inferred from RABD$_{590-765}$ index values show a homogenous distribution with the lowest values within the sediment profile (Fig. 4d). Fe/Mn ratios vary within very low values (mostly below 10). The Mn, Fe, P and Fe/Ti values show high levels with large variability. Extremely low Ca amounts are noted in this zone.

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In Zone II (61-34cm, ~1926-1960), the sediments are dark gyttja, partly laminated with light Ca-rich layers. Green-pigment concentrations slightly increase yet still show little variability. A sharp increase of green-pigments concentrations occurs at 60 cm, and the first two local peaks near 55 cm (~1938) and 48 cm (1945) are notable. Fe/Mn ratios remain at slightly higher values than in Zone I. The Mn, Fe, P contents and Fe/Ti values all decline to low levels and remain relatively stable. Ca counts increase gradually over the whole Zone II.

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In Zone III (34-21.5 cm, ~1960-1977), the sediments are mostly characterized by brown-to-reddish laminations (Mn-Fe rich), with thicker and more distinct laminae contacts than in Zone I. Green-pigment concentrations exhibit much higher values with positive trends, intensified variability, and several maxima (seasonal algal blooms). Fe/Mn ratios first drop in the lower part (34-27 cm) and then continue to increase upward to the top-part of Zone III. Fe, Mn, P, and Fe/Ti values show generally opposing trends to Fe/Mn ratios. Ca contents are elevated during this period relative to Zones I and II.

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In Zone IV (21.5-0 cm, ~1977-2017), the sediments exhibit a clear laminated structure with much more pronounced light calcite layers. The laminations are characterized by a regular succession of light calcite layers (Ca-rich) and dark organic-rich layers (Fig. S4). Green-pigment concentrations display the highest levels with large fluctuations, and reach distinct local maxima at 18 cm (1981), 15 cm (1985), 13 cm (1987), 12 cm (1988), and 8 cm (1997) depths (Fig. 4d). Fe/Mn ratios are at similarly high values as in Zone II, yet with more variability. The Fe, Mn, and P element counts and Fe/Ti all show constantly very low values. The Ca amounts are the highest in the profile and show considerable variability.

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Two principle components, PC1 and PC2 were shown to be significant using a broken stick model. They explain ~35 % and ~30 % of the total variance in the dataset, respectively (PCA-biplot; Fig. S5). The PC1 has strong positive loadings for the terrigenous elements (K, Ti, Rb etc.; Fig. 3 and S6) and thus represents mainly erosional processes related to allochthonous inputs. The PC2 has strong positive loadings for redox-sensitive elements (Fe, Mn), P and Fe/Ti, but negative loadings for Ca, Fe/Mn ratios and green-pigments index values. Therefore, PC2 reflects changes in redox conditions of hypolimnetic water and lake primary productivity. The results of additional PCA analyses zone by zone (Fig. S7b) show that Mn, Fe and P were mostly independent of terrigenous elements (in Zones I to III), however in Zone IV, Mn, Fe and P become correlated with the terrigenous elements. The vertical profile of XRF-P matches very well with the changes of total P concentrations in sediments (Fig. S8). It reveals that XRF-P data can reliably represent qualitative variations of total P concentrations in sediment profiles of Lake Burgäschi.

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4.3 Bulk elements and P fractions in sediment profiles

Sediment TIC, TOC, TOC/TN ratio, S and P fractions also show distinctive features along the four stratigraphic zones (Fig. 5). From the upper part of Zone I (65.2-61 cm; ~1926) to Zone IV, TIC shows a similar pattern to the XRF-Ca contents (Fig. 3 and 5) suggesting that TIC is mostly present in the form of $CaCO_3$. Over the whole profile, TOC/TN ratios are within the range of 9-11. TOC and TOC/TN ratios exhibit mostly similar patterns from Zone I to Zone III. By contrast, total sulfur (S) contents display a different pattern, showing very low values in Zone I and II (mean ~0.5%), and a substantial increase in Zone III and IV.

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The concentrations of relatively labile P fractions (i.e. NaCl-TP, NaBD-TP and NaOH-TP) and total P have a similar trend over the whole profile (Fig. 5 and 6a). They all display rather large values during the upper part of Zone I and generally reduced values in Zone II. In Zone III, the values increase to peaks at ~25 cm depth but sharply decrease to the lowest values in the upper boundary of Zone III and throughout Zone IV. HCl-TP and Ref.-P_o fractions vary differently compared with the other fractions. Low contents of HCl-TP fraction are observed in Zone I and II. HCl-TP fraction has a rather similar pattern as labile P fractions in Zone III, but then it remains at high levels in Zone IV. Ref.-P_o fraction contents show relatively stable values from Zone I to Zone II, followed by a gradual rise in Zone III and in the upper part of Zone IV. The net burial rates (NBR) of P-fraction since 1934 (Fig. S9) show similar trends to the P-fraction concentrations (Fig. 5) (because sedimentation rates MAR are rather constant in core Burg17-C; Fig S9), except for the Ca-P and Ref.-P_o fractions with decreasing NBR throughout the Zone IV.

Regarding the P composition in sediment profiles (Fig. 6, absolute and relative amounts), from Zone I to Zone III (65.2-21.5 cm) NaBD-TP fraction is the most important P-form representing ~50% of total P followed by NaOH-TP fraction. However, in Zone IV (depth above ~ 21.5 cm), HCl-TP becomes the main P fraction (~39% of total P) over NaBD-TP (~30% of total P).

The relationships between response variables and explanatory variables are visible on the redundancy analysis (RDA) biplot (Fig. 7), which, in most cases, correspond well to the results of Spearman rank correlation test (Fig. S10). The relatively labile P fractions (NaCl-TP, NaBD-TP and NaOH-TP) and total P in sediments are strongly positively correlated with redox-sensitive elements (Fe and Mn) and autochthonous Fe (Fe/Ti). However, these P fractions are negatively related to hypolimnetic oxygenation proxy (Fe/Mn ratios) and, to some extent, to lake productivity indicators (green-pigments, XRF-Ca and TIC). HCl-TP and Ref.-P$_o$ fractions are positively correlated. However, only HCl-TP fraction has close positive relationships with lake productivity indicators.

5 Discussion

5.1 Trophic state evolution of Lake Burgäschi

Four main phases of different lake trophic levels (based on RABD$_{590-765}$ index values) were distinguished since the early 1900s, as summarized in Fig. 8 and Fig. S11. During the period prior to ~1926 in Zone I, the lowest green-pigments index values reflect low lake primary productivity. In the early 1900s, agricultural impacts around the catchment area of Lake Burgäschi were not prominent (Guthruf et al., 1999). It can be expected that the lake had low nutrient loads from the catchment drainage during this period. Lake Burgäschi is classified as naturally oligotrophic based on morphometric parameters (LAWA, 1998) and as naturally mesotrophic according to Binderheim-Bankay (1998). Therefore, at the times of Zone I, Lake Burgäschi was likely in low trophic levels with a possible oligotrophic-mesotrophic condition.

The transition to Zone II (~1926-1960) was marked by generally increased sedimentary green-pigment concentrations and CaCO$_3$ contents (Fig. 3, 4d and 5), respectively, indicating enhanced lake primary productivity. The slightly decreased TOC/TN ratio also suggests a rise in autochthonous organic matter proportion (Meyers and Ishiwatari, 1993). The first two algal blooms (peaks of green-pigments index; Fig. 4d) imply a very likely mesotrophic to eutrophic state of the lake. Indeed, the study of Büren (1949) revealed that in 1943-1945, the trophic state of Lake Burgäschi had already shifted between mesotrophic and eutrophic. Interestingly, the water-table lowering during 1943-1945 (Guthruff et al., 1999) with related enhanced drainage of intensive agricultural fields and meadows (Büren, 1949) did not seem to have had an immediate impact on lake primary productivity (Fig. 3).

In Zone III (~1960-1977), continuously increasing green-pigment concentrations and several algal bloom events reveal strong positive trends in lake eutrophic levels. The significant eutrophication in Lake Burgäschi might have caused intensified CaCO$_3$ precipitation (TIC) and sulfur (S) contents in sediments (Fig. 4a and 5), which is in agreement with the findings from many other eutrophic lakes (Holmer and Storkholm, 2001; Bonk et al., 2016; Schneider et al., 2018).

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During Zone IV (1977-2017), we interpret that Lake Burgäschi was in highly eutrophic conditions, based on constantly high green-pigments index values and multiple prominent algal blooms (Fig. 3). Low and decreasing TOC/TN ratio values (< 10) in this zone suggest a dominant source of organic matter in sediments from aquatic primary production, which has been interpreted as a signal of eutrophic waters (Enters et al., 2006). Our interpretation is further supported by high chlorophyll-*a* concentrations in surface waters (>8 ug L^{-1}; GSA, 2007) and the dominance of blue-green algae in the phytoplankton biomass during 1977 to 1992, which characterized Lake Burgäschi as highly eutrophic (GBL, 1995; Guthruf et al., 2013).

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5.2 Reconstruction of hypolimnetic oxygenation regimes of Lake Burgäschi

A large number of studies have used the proxy of Fe/Mn ratios in sediments to reconstruct past water oxygenation and mixing regimes of the lake, such as Mackereth (1966), Frugone-Álvarez et al. (2017), and Żarczyński et al. (2019) etc. However, this proxy and its interpretation are limited to cases in which the annual cycle of Fe and Mn deposition in lakes is mostly driven by redox changes in the hypolimnion and related diagenetic processes in surface sediments instead of driven by terrestrial inputs (Boyle, 2001; Naeher et al., 2013). In Lake Burgäschi, during Zone I to III, Mn and Fe were mostly independent of erosion indicators as shown in Fig. S7b. Furthermore, Van Raden (2012) has revealed that the presence of Mn-rich laminae in sediments of Lake Burgäschi can indicate frequent short-term wind-induced mixing events in the lake. Therefore, we suggest that the deposition of Fe and Mn during these three zones was mainly controlled by in-lake processes. Fe/Mn ratios together with Mn precipitation reliably track past changes of hypolimnetic oxygenation of Lake Burgäschi.

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In Zone I (pre ~1926), the sediments feature well-preserved Mn-Fe rich laminations and very low Fe/Mn ratios (Fig. 3 and 4a), suggesting that the lake hypolimnion was seasonally well-oxygenated. The similar occurrence of visible Mn-and Fe rich laminae in sediments were also reported by Rey et al. (2017) in Lake Burgäschi and from other lakes, for example, Lake of the Clouds in the US (Anthony, 1977), Lake Cadagno in the Swiss Alps (Wirth et al., 2013), and Lake Żabińskie in Poland (Żarczyński et al., 2018). They revealed that the red-orange Mn-rich layers mostly consist of authigenic rhodochrosite (MnCO$_3$) that was formed when Mn-rich anoxic bottom waters are mixed with oxygenated surface waters for short intervals. The preservation of this Mn-rich layer is only possible when its sedimentation process exceeds the release process under anoxic hypolimnetic conditions (Stevens et al., 2000). Therefore, during this period, short-term mixing events and associated oxygenation may have occurred during overall stratified or anoxic conditions in the hypolimnion.

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In Zone II (~1926-1960), the higher Fe/Mn ratios and very low Mn- and autochthonous Fe (Fe/Ti) amounts are interpreted as the results of stable anoxic hypolimnetic waters. The formation and preservation of Fe-and Mn-oxides in sediments is largely prevented under long-term stratification/reducing conditions (Stevens et al., 2000). The lake most likely developed anoxic hypolimnetic conditions with yearly incomplete or missing circulation in the hypolimnion.

In Zone III (1960-1977), overall decreased Fe/Mn ratios combined with reappearing Mn-and Fe-rich laminations reflect better short-term oxic conditions in hypolimnetic waters than in Zone II. However, during ~1970 to 1977, Fe/Mn ratios gradually increased (Fig. 3), which points to less oxic conditions in the hypolimnion. It seems to be related to synchronously progressive lake eutrophication (see Sect. 5.1). Higher primary productivity and

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strengthened anoxia in the hypolimnion are commonly observed in stratified lakes (Giguet-Covex et al., 2010; Mikomägi et al., 2016). Higher lake primary productivity increases high-rate aerobic degradation of organic matter and, consequently, oxygen-depletion in the hypolimnion and sediments (Gächter and Müller, 2003; Nürnberg, 2007).

Finally, in Zone IV (1977- 2017) Fe/Mn ratios proxy is no longer valid to indicate hypolimnetic oxygenation regime, as suggested by predominantly terrestrial sources of sediment Fe and Mn (Fig. S7b). Nevertheless, the well-preserved laminated sediments during this period are a clear sign of absent benthic bioturbation and thus represent an indicator of generally strong anoxic conditions in hypolimnetic waters, occurring simultaneously with a highly eutrophic period. According to the limnological monitoring data of Lake Burgäschi between 1978 and 2007 (GSA, 2007), the lake water was completely anoxic at depths below 20 m during the summer-autumn stratification; even during winter circulation of most years, the lake water was still not completely mixed.

5.3 Phosphorus composition and factors controlling long-term P-fraction retention in sediments

Prior to 1977 (i.e. Zones I-III), NaBD-TP (redox-sensitive Fe- and Mn bound P) and NaOH-TP (partly non-reducible Fe oxides-P) fractions were the primary P forms in sediments of Lake Burgäschi (Fig. 6 and 8). This seems to compare well with the study of Moosmann et al. (2006), who suggested that sediment Fe contents control P retention in sediments of the Swiss Plateau lakes. However, after ~1977, we observed a change to predominantly Ca-P (apatite-P), occurring concurrently with the operation of hypolimnetic withdrawal restoration. This clear pattern in sedimentary P-fraction change can be largely attributed to this restoration measure. The hypolimnetic withdrawal treatment in Lake Burgäschi removes not only hypolimnetic P but also dissolved metal (Al, Fe and Mn) ions and, thus leads to calcite as the main sorbent for P in upper waters and to an enhanced proportion of Ca-P fraction in sediments.

In spite of the effects of lake restoration on sedimentary P retention in Zone IV, overall, the retention of total P and labile P fractions in the sediment profile was mainly controlled by autochthonous Fe (Fe/Ti), Mn, and hypolimnetic oxygenation proxy-Fe/Mn ratios, as shown by the results of RDA analysis (Fig. 7). Our results support the previous suggestion that long-term permanent sediment-P retention is largely limited by the sediment's binding capacity in anoxic conditions (Moosmann et al., 2006; Hupfer and Lewandowski, 2008), which, specifically in our case, is determined by redox-sensitive elements (autochthonous Fe and Mn) preserved in sediments. These findings are discussed in the context of each cluster zone as follows: During Zone I and Zone III, when the hypolimnion had better seasonally oxic conditions (see Fig. 8 and Fig. S11), the increased retention of Mn and Fe, and labile P fractions occurred simultaneously (Fig. 3 and 5). This phenomenon might be caused by efficient P-trapping in Mn- and Fe enriched layers. It has been suggested that the formation of laminated Mn- and Fe enriched layers could serve as a protective cap to reduce P release from surface sediment layers to the anoxic hypolimnion (Żarczyński et al., 2018) which, thus, can help improve P retention within these sedimentary layers. In Zone II, small amounts of labile P fractions might result from decreased P-bearing solid phases (Mn and Fe minerals) in sediments under anoxic conditions in the hypolimnion (see higher Fe/Mn ratios in Sect. 5.2; Fig. S11). However, in Zone IV, we observed the lowest retention and NBR of total P and labile P fractions in recent

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sediments (Fig. 5; Fig. S9). We interpret this as a combined result of eutrophication-induced hypolimnetic anoxia and hypolimnetic withdrawal since 1977 whereby P-rich hypolimnetic water is discharged out of the lake. On the one hand, under stable anoxic conditions in the hypolimnion caused by strong eutrophication, reduced Mn and Fe preservation (Fig. 3) suggests a low capacity of permanent P-trapping within the anoxic sediments. On the other hand, hypolimnetic withdrawal restoration in Lake Burgäschi has substantially reduced hypolimnetic P concentrations by a factor of 5-6 since 1978 (Fig. S11; GSA, 2007) and MARs (Fig. 2c and Fig. S9). This indicates a concomitant decrease in sediment-P release to the hypolimnion and P sedimentation to the water-sediment interface (gross sedimentation of P) as well. Consequently, decreased total P concentrations and total P-NBR in sediments were observed (Fig. 6a and S9). The reduction of total P contents in upper sediments caused by hypolimnetic withdrawal was also reported from Lake Kortowskie of Poland (Dunalska et al., 2007). Moreover, our findings confirm that this restoration is an effective method to reduce sediment-P release potentials, as indicated by considerably decreased NBR of labile P fractions in upper sediments (Fig. S9).

In the whole sediment profile, HCl-P and Ref.-P_o fractions had mainly autochthonous origins and were mainly controlled by in-lake processes rather than by clastic inputs (e.g. apart from molasses sandstone), as indicated by absent positive correlations between the two fractions and detrital elements such as Ti, K and Al (Fig. 7). HCl-P (i.e. Ca-P) fraction retention, to a large extent, resulted from authigenic $CaCO_3$-P precipitation, and increased with higher eutrophic levels in Zone III and IV (Fig. 5; Sect. 5.1). We interpret this as an incidence of biologically driven co-precipitation of Ca and P in highly productive lakes. The phenomenon of Ca-P co-precipitation has been observed and studied in many calcareous lakes (Dittrich and Koschel 2002; Whitehouse, 2010), and is assumed to be responsible for the scavenging of dissolved P from surface waters of eutrophic lakes (Hamilton et al., 2009). In addition, large amounts of Ca-P in surface sediments (top 21 cm) can act as a potential negative feedback to eutrophication in Lake Burgäschi, because Ca-P fraction is relatively stable in sediments and has low potentials of P-release from surface sediments back to lake waters. Interestingly, HCl-P fraction retention and NBR in sediments of Zone IV were generally lower than in Zone III (Fig. 5 and Fig. S9), although the lake in Zone IV had relatively higher eutrophic levels (see Sect. 5.1; Fig. S11). The pH in the hypolimnion of Lake Burgäschi varied between 7.0 and 7.5 according to the monitoring data in 1993, 2003, and 2013 (Guthruf et al., 2013). Therefore, the acid dissolution of Ca-P in the hypolimnion and at the water-sediment interface is small and unlikely significant during Zone IV. The generally decreased retention and NBR of Ca-P fraction were seemingly related to hypolimnetic withdrawal, which has caused lower water-P concentrations and MAR of sediments as discussed above. As a result, there are reductions of $CaCO_3$-P co-precipitation in the epilimnion and consequently of Ca-P net sedimentation in surface sediments. Overall, Ref.-P_o fraction retention and NBR in the sedimentary profile show less variability compared with other P fractions (Fig. 5 and Fig. S9). Nevertheless, the lower NBR of Ref.-P_o fraction in the upper sediments (~ top 10 cm) could be derived from the ongoing early degradation of fresh organic matters.

The interesting observation is that the water-P reductions caused by the hypolimnetic withdrawal in Lake Burgäschi (GSA, 2007; Nürnberg, 2007) have been ineffective in reducing algal blooms and curbing eutrophication. Similar findings were also reported from some lakes in Europe and the US (Kosten et al., 2012; Kolzau et al., 2014; Fastner et al., 2016). These authors have attributed this phenomenon to insufficient external P-load reduction, higher water temperatures under global warming of the last few decades, and the light or nitrogen

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limitation of surface-water phytoplankton. In Lake Burgäschi, phytoplankton growth in the trophic zone is still limited by P after 1978 rather than by the nitrogen (GSA, 2007) as the nitrate concentrations stay as high as 0.5-3 mg N / L in the upper 5-m waters. Hence, we suggest that these factors mentioned above, except for nitrogen limitation of lake productivity, may also contribute to promoting persistently high primary productivity in Lake Burgäschi. But the main driver keeping productivity high, is the continuing high external P loads from the lake catchment. During summer stratification, the high loads of P into the lake epilimnion primarily support phytoplankton growth in the photic zone, which is not strongly influenced by the hypolimnetic-P discharge and internal P loadings. From a management perspective, it is still critically important to focus on lowering external P loads in order to decrease primary production and eutrophication in seasonally-stratified small deep lakes which are more likely to favor stable stratification during phytoplankton growth season.

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6 Conclusion

This study shows that in Lake Burgäschi, more than half of sediment P is buried in relatively labile P fractions (Fe/Mn/Al-P), yet with low potentials for P-release from these labile P fractions in deeper layers (below ~21 cm). Our results highlight the importance of hypolimnetic oxygenation/mixing regime in controlling long-term P retention and net burial rates of labile P fractions in sediments of this small deep lake. Irrespective of increasing lake primary productivity during early 1900s to 1977, the two periods of high sedimentary retention of total P and labile P-fraction occurred in Fe- and Mn enriched laminae, which appears to be linked to seasonal mixing of the hypolimnion in the past. Importantly, the positive effects of hypolimnetic withdrawal in Lake Burgäschi were observed primarily in sediment P-fraction data but not in lake trophic state. The 40-year operation of hypolimnetic withdrawal has impoverished sedimentary P, in particular largely decreased net burial rates of labile P fractions (potential internal P loads), and increased the relative proportion of stable Ca-P fraction in top sediment layers (0-21 cm). Nevertheless, the lake is currently still highly eutrophic. We attribute the delay of lake recovery primarily to still high nutrient inputs from the nearby or surrounding agricultural area into the lake trophic zone during stratification seasons. This study calls for consistently more effective measures to minimize external P loadings from the catchment, such as optimizing fertilizer application practices and technical measures in the drainages.

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Data availability

The data will be made available at PANGAEA at https://doi.pangaea.de/10.1594/PANGAEA.908896.

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Author contributions

L.T. helped with sample collection, analyzed the sediment, conducted data analysis, wrote the manuscript, and acquired most of the funding for the project.

P. Z. helped with sediment core subsampling, conducted the hyperspectral imaging (HSI) scanning, helped with XRF-scanning, substantially contributed to the data interpretation.

S.S. measured gamma-spectroscopy radiometric activities, generated the data for chronology and helped with data interpretation.

R.L. conducted the XRF-scanning and helped with data interpretation.
M.G. designed the study, helped discussing the results, editing the manuscript and supervised the project.
All authors commented on the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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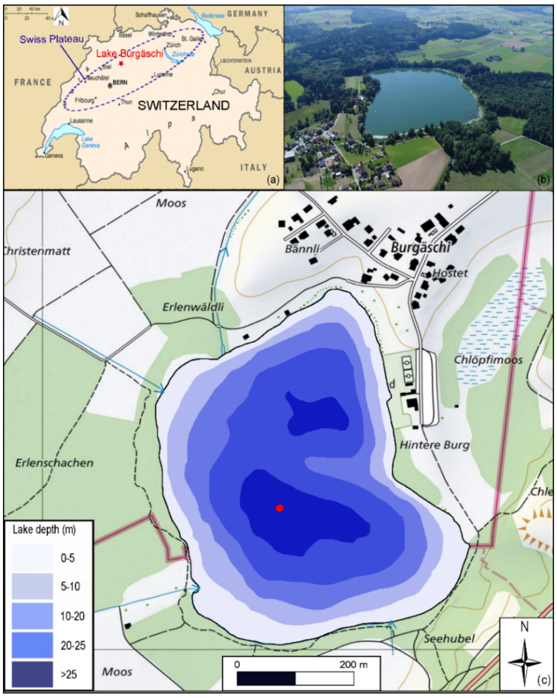

Figure 1: Study site. (a) Overview map of Switzerland and the Swiss Plateau. Lake Burgäschi is indicated as the red asterisk. (b) Photo of Lake Burgäschi and catchment (© 2018 Google Maps). (c) Bathymetric map of Lake Burgäschi adapted from Guthruf et al. (1999). The red dot indicates the coring site (color figure online). Green areas around the lake indicate forests, white areas agricultural lands. Inflow and outflow to the lake are indicated by blue arrow lines (topographic maps: © swisstopo).

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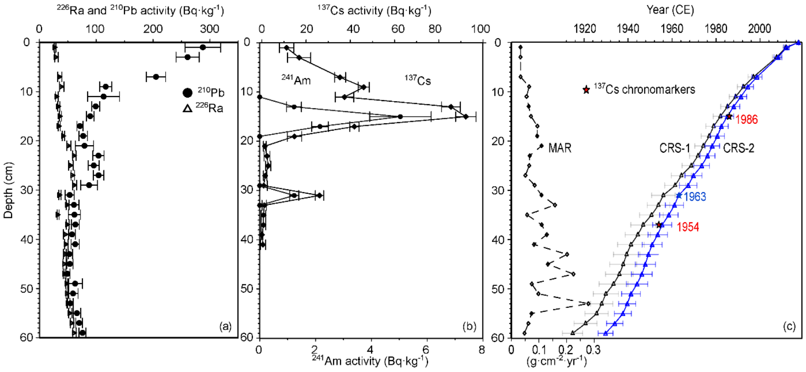

Figure 2: (a) Total ^{210}Pb, ^{226}Ra, and (b) ^{137}Cs and ^{241}Am activity concentration profiles in sediment core Burg17-B from Lake Burgäschi; (c) The comparison of different ^{210}Pb CRS models: unconstrained CRS-1 model and constrained CRS-2 model at 1963; the mass accumulation rates (MAR) are obtained from the CRS-2 model.

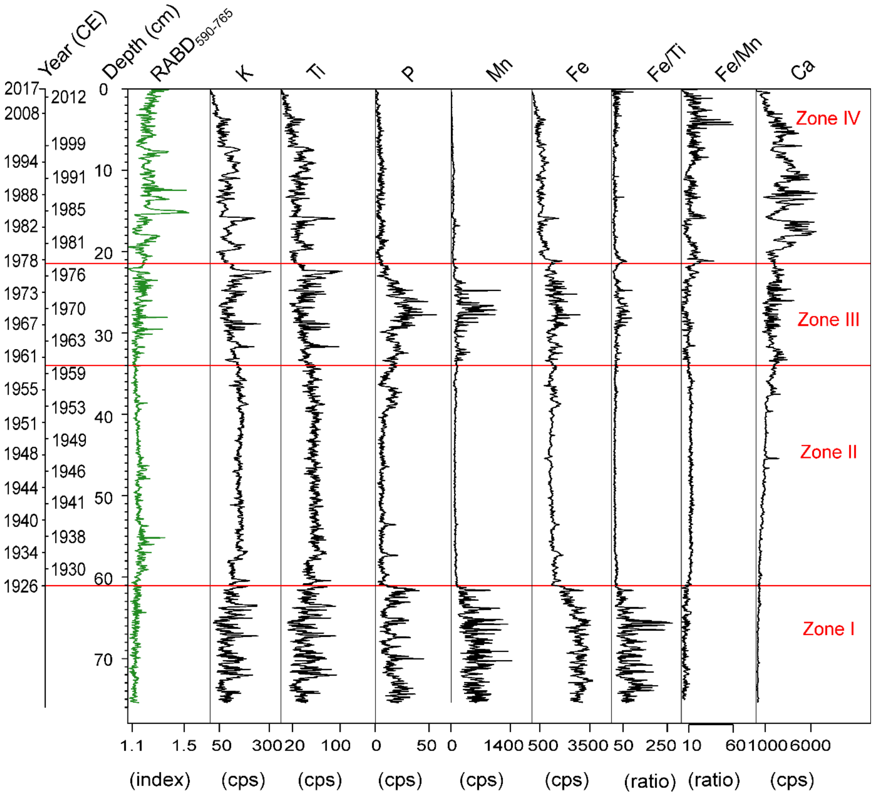

Figure 3: Stratigraphic records of HSI-inferred green-pigments (RABD$_{590-765}$) and XRF-data in sediments of core Burg17-B. Elemental counts are represented in cps (counts per second). The red horizontal lines separate the four significant clusters retrieved by the CONISS analysis (color figure online).

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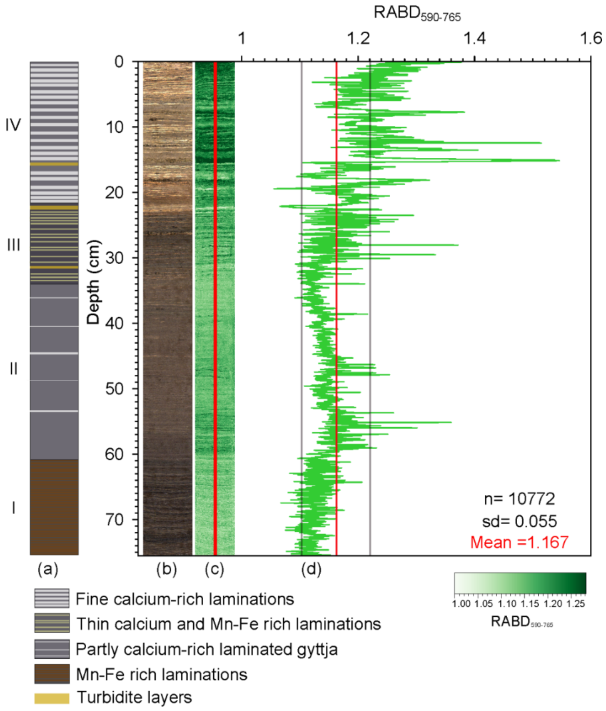

Figure 4: (a) Lithological description of Burg17-B sediment core. The intensities of Ca, Fe and Mn in each unit were inferred from XRF-element counts in Fig. 3; Yellow colors highlight the turbidite layers identified from the XRF peaks of siliciclastic elements e.g. K, Ti, and Rb. (b) RGB contrast enhanced sediment core picture. (c) The map of the spectral index RABD$_{590-765}$ (i.e. green-pigments) distribution, and (d) the graphic output of RABD$_{590-765}$ spectral index within the boundary of the red lines (c) which shows the 2-mm wide sampling range. The red line in (d) indicates the mean index value and the grey lines represent the one-standard deviations (sd). The colorbar represents the index values of the distribution map (color figure online). n is the number of rows of the RABD$_{590-765}$ index map.

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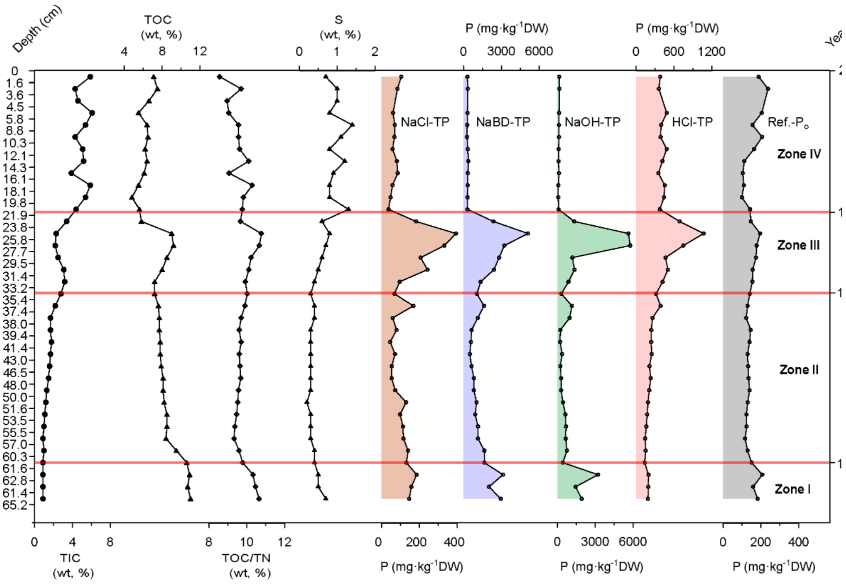

Figure 5: The stratigraphy of total inorganic carbon (TIC), total organic carbon (TOC), sulfur (S) contents, TOC/TN ratio and five phosphorus fractions in sediments of Lake Burgäschi. The y-axis (left) refers to the sediment depth of core Burg17-B. The horizontal red lines separate the significant CONISS zones as in Fig. 3. The secondary y-axis (right) indicates approximate ages of sediments inferred from the Burg17-B core chronology.

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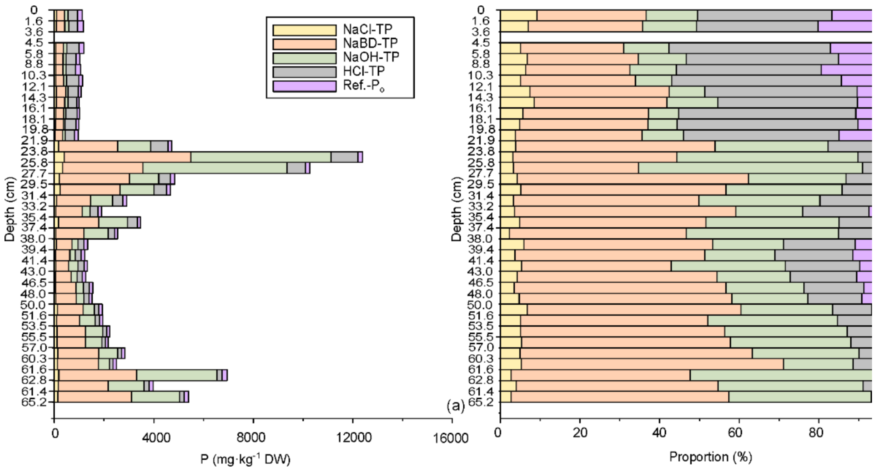

Figure 6: Vertical profile of (a) P fractions concentrations and (b) their proportions of total P in sediments. The y-axis (left) refers to the sediment depth of Core Burg17-B. Note that the sample between 3.6-4.5 cm depth was removed from dataset because the values were extremely higher than any sample data (data not shown), which is abnormal according to XRF-P counts at the corresponding depth (Fig. S8b). We attributed this to the result of contamination during the sample measurements.

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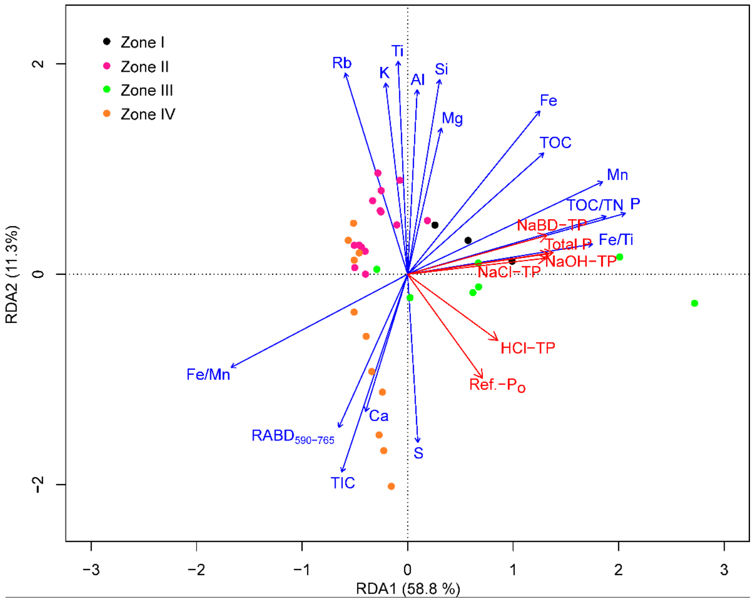

Figure 7. RDA biplot displaying correlation between response variables (P fraction dataset; red arrows) and explanatory variables (green-pigments and other geochemical records; blue arrows). The colored points represent data points of individual cluster zones in Fig. 3, 5 and S6.

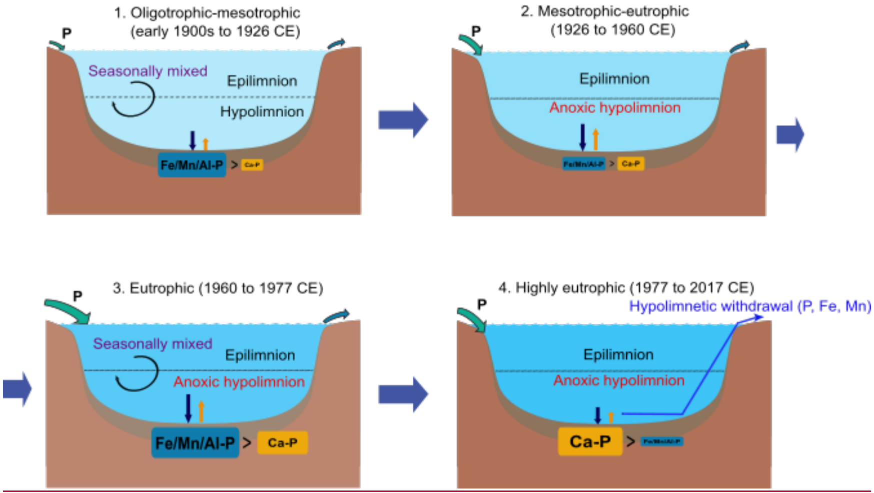

Figure 8: Conceptual diagram, summarising the inputs/outputs of phosphorus (P), hypolimnetic withdrawal restoration, lake trophic levels, mixing regime and phosphorus (P) fractions retention in sediments of Lake Burgäschi during four stages/zones. Note that the illustrated sizes of P fractions (Fe/Mn/Al-P and Ca-P) among different stages overall indicate the relative amounts of P fractions in sediments.