Steinsberger et al. investigate the flux of reduced substances (Fred) from sediments in five deep lakes of different trophic states. They found no indication that the trophic state of the lakes controls Fred. However, organic carbon mass accumulation rates together with the mean hypolimnion depth of the lakes relate to Fred and can potentially be used to estimate the influence of Fred to O2 consumption in eutrophic deep lakes. The authors collected a big dataset from five deep lakes and calculate/estimate some factors that are relevant for assessing the hypolimnetic O2 consumption and its driving factors.
The overall topic of the paper falls into the scope of Biogeosciences and it presents some novel and a solid dataset to assess the fluxes of reduced compounds from sediments and its role for hypolimnetic oxygen consumption. The overall presentation of the methods and results/discussion could be improved. The whole manuscript seems lengthy and quite descriptive at many places. I will elaborate on this in more specific comments below.

I would recommend a publication but only after a rewriting of the aims/hypothesis and methods and a restructuring of the discussion to strengthen the main messages.

Major comments:
1) The aims of the paper could be reformulated to increase the curiosity of the reader. As it is now, the aims are: extend a dataset/assess constraints/discuss spatial variabilities and consequences: : : This is also reflected in the results/discussion section that is often hard to follow and difficult to say what the authors want to say/conclude here.

The motivation of this work was the observation in a broad variety of lakes that the areal hypolimnetic mineralization rate (AHM) in highly productive lakes could be explained by two components: the O_2 consumption at the sediment-water interface, and the O_2 consumption by reduced compounds diffusing from the sediment (Müller et al., 2012). In this follow-up project, we focused on the factors that control the fluxes of reduced compounds (methane, ammonium, iron and manganese). Therefore, a large set of porewater fluxes had to be acquired from several lakes with different trophic states, different depths and seasons. Such a laborious work was only possible due to a newly developed method (Torres et al., 2013) allowing on site analyses. The driver for the fluxes of reduced substances was found to be the mass accumulation rate of organic carbon in the sediments. With this heritage from eutrophic times in the sediments we explained the delayed reaction of AHMs in spite of improvements in the TP concentrations of (formerly) eutrophic lakes. In addition, we document that O_2 consumption due to reduced substances decreased with mean lake depth, which explains that even in highly productive lakes (such as Lake Geneva) the freshly settling organic matter is well decomposed due to the still elevated deep water O_2 concentrations. Thus, TOC mass accumulation rates are small leading to only very small production of reduced compounds in the sediment.
As the reviewer states correctly, gathering a large porewater data set and finding a common driver were indeed the aims of this manuscript which we state on P2 L 22-29.
In order to improve the manuscript we kindly ask the reviewer to clearly pinpoint the sections that need improvement.

The first two paragraphs in the "Results and Discussion" (page 5) are only data descriptions without any interpretations jumping from one lake to the other.

I got easily lost in the details and did not get the major results and their interpretation, something that I would expect at the beginning of this section. I would suggest to reformulate the aims and maybe try to formulate a hypothesis (or hypotheses) or expectations from the data and analyses. With those newly formulated hypotheses the "Results and Discussion" section should be rewritten/-structured, focusing on the new hypotheses.

2) The "Materials and Methods" description has missing information:
How many cores were taken per day and depth? I am confused because the authors talk about a "set of cores" collected in Lake Zug (p. 3 line 2).

Was there any replication or does this refer to the three cores taken for all analyses including reduced substances via capillary electrophoresis, methane and water/TOC content?
In the introduction, the authors talk about 50 cores that they took (p. 2 line 21). When I count one core per date and depth for the five lakes (Table 1), I get to 57 cores, which means no replication. How reliable are those data without replication?

And what happened to the 7 cores that do not match with the number stated and my calculations?

It would also be nice to read somewhere how many times the reduced substances via capillary electrophoresis, methane and water/TOC content in each core were measured and to what depth.

We agree that this is not entirely clear. Concerning the porewater analysis, we propose to modify the text as follows: "Each porewater sample was analyzed once with two capillary electrophoresis devices each equipped with a capacitively coupled contactless conductivity detector (CE-C^{4}D) (calibrated for anions and cations) directly at the lake shore. (p.3 l.21-23)
Concerning the methane analysis, we propose to add the following sentence: "The headspace of each CH$_4$ sample was analyzed three times by gas chromatography (Agilent) using a 1010 Supelco Carboxene column with a standard deviation of 0.1 % to 1.3 %." (p.4 l.1-2).
The depth of the porewater samples can be seen in Fig. 1 and varied between lakes. The lowest sampling depth was at least 20 cm, which was sufficient to calculate fluxes. All sediment parameters were measured until the lower end of each core, which varied between 30 cm and 55 cm. Yet for the calculation of e.g TOC-MAR we only evaluated the top 10 cm of the sediment.

The distances of the holes are mentioned I could not figure out how deep the sediment was, only from looking at figure 1. From Figure 1, I can also see that it has different numbers (by counting dots) and sometimes different depths and that the distances between points change. This is not mentioned at all in the method description.

The length of sediment cores was between 20 cm to 55 cm, however, this has no effect on the porewater profiles, which are depicted in Figure 1. The spatial resolution of porewater sampling can also be seen from Figure 1, and we think it is not helpful (nor required) to list porewater sampling depths explicitly for all cores. However, we agree that a general statement of the sampling resolution is useful and propose to add the following sentence: "The sampling resolution was 5 mm for the first 5 cm of sediment, ≤ 1 cm between 5 cm and 10 cm of sediment, ≤ 2 cm between 10 cm and 20 cm of sediment and ≤ 3 cm below 20 cm of sediment". (p.3 l.18-20).

I would like to see a photograph of the cores with the holes, maybe added to the supplement. That would make it much easier to picture such cores.

We see no benefit showing a picture of a PVC tube filled with sediment within this manuscript. Such a picture is presented on the journal cover page of Environmental Sciences – Processes&Impacts Vol. 15/4 (2013) where Torres et al. (2013) was published: (http://pubs.rsc.org/en/content/articlepdf/2013/em/c3em90008h?page=search)

A short description about the literature search in the main text would be helpful. How did the authors search for those data and what did they extract and did they all use similar methods?

We cited the literature that we considered essential, illustrative and supportive for the subject. If we were ignorant about some colleagues' work we are very grateful if you let us know.

3) Assessment of uncertainty of data: The authors provide only limited information on the range of their data. I already asked the question if the authors replicate the sampling at one point on one sampling day and if not how reliable the data are. In figure 1, there are ranges of the data and you can see that especially at the deepest points, there are wide ranges. But in table 2, there is only one value. Did the authors calculate averages for the sampling times? Or are these data from only one sampling time? It is hard to assess the variability of the data at each sampling point without any knowledge of variation or uncertainty analysis. The authors do not test their results!

The reviewer touches an import topic. As no replicate porewater analyses on more than one core could be made, it is not possible to directly determine the variability of the porewater data. All measurements were carefully performed and the CE instrument was calibrated each time before and during the porewater measurements and checked against the cited multi ion standards with deviations <5% (p.3 l. 24-27). Torres et al. (2013) showed that porewater measurements performed by CE compared to measurements performed by standard ion chromatography yielded similar results. Further, as previously mentioned our data closely agree with earlier studies (Urban et al., (1997), Maerki et al., (2009) and Müller et al., (2012). Therefore, we are confident that the data presented shows state of the art porewater analysis. Local sediment heterogeneity is a matter of constant debate and could not be quantified with the presented experimental investigation. It cannot be decided to what extent the variations in the porewater concentrations were caused by local heterogeneity or temporal variation. We address this issue on p.4 l.8-13. We changed Fig. 2 and now show the average F_{red} values as well as all F_{red} values measured in the lakes.

Values given in Table 2 show the average flux of a reduced species calculated over all observed values. We will add a sentence to the table to clarify the matter: "Porewater fluxes are averaged over all flux measurements of each individual species".Further we will add the standard deviation of the flux measurements and the F_{red} calculation for Lake Baldegg and Lake Aegeri. Only for those two lakes we have enough data to justify showing variations.
In addition, seasonality of the fluxes is an important issue, however, this goes beyond the scope of the present manuscript. It will be treated and discussed in a follow-up modeling paper, which is in preparation.

4) I miss some references throughout the text:
p. 2 line 5: "This relationship suggested a constant fraction of O2 consumption from the sediments, which agreed with the few available estimations from direct of sediment porewater measurements of reduced compounds (ref.)

The entire text from page 2, line to line 12 refers to work done by Müller et al. (2012a). The reference is cited twice in this paragraph, and we think it is not necessary to cite it a third time after this sentence.

p. 3 line 17-21: a reference for the headspace technique?

In the present literature methane sampling from sediment cores and subsequent analysis from the headspace is described as we do it in this manuscript (e.g. Sobek et al., 2009, Randlett et al., 2015). This is sufficiently clear and comprehensible. We prefer not to refer to other references that describe the same procedure the same way as we do it here.

p. 4 line 26: "The lower TOC-MAR calculation depth of 10 cm was chosen to remain within the timeframe were steady state conditions can be assumed (ref.)."

That is our rational for TOC-MAR calculation in section 2.5. Just recently (after manuscript submission) a paper was published on a related theme by Radbourne et al. (2017). We propose to add a citation to this paper here.

p. 7 line 17-19: "The areal accumulation of TOC per time is controlled by gross sedimentation (which is related to primary production), O2 concentration in the lake bottom water, biological factors like grazing and bioturbation, and physical parameters such as sediment focusing (ref.)." Or is this results taken from the author's own data?

We propose to add here a reference to Sobek et al. (2009), which is already cited at other locations in the text.

5) Why did the authors install the sediment traps at 15 m water depth? All sampling points of the cores are at deeper points and the sedimentation can change with deeper waters, especially because 15 m water depth is above the hypolimnion in most lakes. Does this influence the data and conclusions? Does it play a role and if yes, how? Please also consider discussing this in the main text.

Sediment traps were installed both at 15 m water depth, and at 1 m above the bottom at the deepest location of the lake. The upper traps were used to estimate net export of OC from the productive epilimnion to the deep hypolimnion. They were below the temperature gradient (the metalimnion) at all times.
For the calculation of burial efficiency, only the observations from the lower sediment traps were used and therefore the calculations are independent of the upper sediment trap.
We added a sentence in section 2.3 as follows to clarify this: For the calculation of the gross sedimentation only data from the lower trap was used. (p.4 l.21)

Minor points: - P. 2 line 4: : : :from direct sediment porewater: : : Delete "of"!

We agree

- P. 5 line 4: in the four lakes : : : No capital letter!

We propose to change this to it to "the four lakes, Lake Baldegg, Lake …"

- P. 8 line 3: do you need to say "from the sediments were virtually zero"? Do the authors refer to both lakes that they mention before or only one here?

Yes, this statement refers to both lakes. We propose to change the expression to "close to zero".

- P. 10 line 3: "more commonly available than"

We agree

Reviewer 2

The paper by Steinsberger et al presents interesting results on the role of dissolved fluxes from sediment in the oxygen consumption in lakes with oxic hypolimnion. It fits perfectly one of the scopes of the journal, linking mainly chemical and physical aspects of the cycle of chemical substances, organic matter, and sedimentation rates. The paper presents new data from fives Swiss lakes with different trophic status. Results, interpretation and conclusion seem coherent, however my main comment concerns i) the lack of clarity in the presentation of the results, and their use in figures. For instance 8 cores were collected in Lake Geneva with corresponding Fred, but only one point plotted (and discussed?) on figure 2 and 3 (average value, deepest point?).

We thank the reviewer for mentioning the problem. We measured the porewater concentrations in eight different cores in Lake Geneva but no cores for TOC measurements nor dating were retrieved. Therefore we relied on the cited data to calculate one average TOC-MAR value for the deep basin of Lake Geneva (p4 l.9-15). As F_{red} was rather similar at all sampling stations (below >0.1 gO$_2$ m^{-2} d^{-1}) and varied only between 0.02 and 0.09 gO$_2$ m^{-2} d^{-1} we decided to plot only one averaged F_{red} value with that average TOC-MAR value. However, we agree with the reviewer that this is unclear and therefore propose to plot all F_{red} values of Lake Geneva into Fig2 and Fig3. But we will not discuss the individual points in the text, as F_{red} was similarly low at all sampling stations.

I have the general feeling that a large set of data has been produced, but partly discussed; and ii) how the variability in the observed fluxes is taken into consideration in the final assessement. On page 5 line 14 and following, the authors correctly indicate that fluxes, at the same location, show variations due to local sediment heterogeneity and/or seasonal effect. Depending on the substances, values varies between 23% to 67%. However, only one value per lake /depth is given in table 2, without any uncertainty, either from the measurements themselves (including uncertainty in sediment accumulation rates) or from the replicates. Then how the values in table 2 are computed (simple average, time weighted)? What could have these uncertainties on the interpretation and conclusion? From a quick evaluation it seems that the main trends are still significant, but this should be discussed in the manuscript to improve the strength of the conclusion.

In table 2, we show average values of all flux measurements at a single sampling station. We agree that it makes sense to present the variability of observations, and therefore propose to add the standard deviations of the flux measurements and F_{red} for Lake Baldegg and Lake Aegeri. Only in these two lakes enough measurements were conducted to justify the calculation of a standard deviation. We also propose to modify the text accordingly. As no duplicate sediment cores were taken, it is not possible to show the variability of the individual flux measurements.

We further propose to add all F_{red} values to Fig.2 to show the encountered variability and to modify the text accordingly. The uncertainties, although considerable, do not change the interpretation or conclusion of the data. At the moment, we are preparing a paper in which we try to explain the encountered seasonal variations with a modelling approach. We believe that incorporating a discussion about the seasonal variations would be beyond the scope of this manuscript and would dilute the main findings of this study.

More detailed comments:

Page 2 line 31. From the classical reference (Wetzel 2001), Lake Geneva is meso-eutrophe (10-30 mg/m3) based on phosphorus content (20 mg/m3), but also on chlorophyll (.

We agree and propose to change this to "meso-eutrophic".

P4 line 23. I don't understand why the sedimentation rate (SR) is calculated based on a depth scale, and then at each layer a TOC-MAR (mass accumulation rate) is
calculated, including porosity and dry density. This way is correct if the porosity is relatively constant downcore. But in general in recent sediment porosity vary strongly with depth, and this variation should be taken into account before the computation of the sediment rate. For instance a SR of 2 mm/y correspond to 0.05g cm/2/y with 90%porosity, but 0.1 g/cm2/y with 80% porosity.

We agree that sedimentation rates likely vary downwards. Yet the sedimentation rates over the range of 2-10 cm sediment depth do not change drastically. Based on the characteristic ^{137}Cs peaks of 1986 and 1963 the sedimentation rate of the top 10 cm can be well established. In Lake Hallwil, no variation in the sedimentation rate over this part of the sediment can be seen. In Lake Aegeri and Lake Baldegg additional to ^{210}Pb and ^{137}Cs dating, varve counts over that sediment range were also evaluated and agree well with sedimentation rates previously published (e.g Lotter et. al (1997).
The porosity was calculated for each sediment interval separately with the individual water content and density. The density itself was calculated by the empirical relationship between TOC content and pure geogenic material (Och et. al (2012). We propose to add a section to clarify this and further add the equations for dry density and porosity calculations (p.5 l.10-16).

P4 line 24. It is not clearly explain here (but discussed later) why the surface sediments are excluded from the computation.

We explain this in the ensuing sentence p.5 line 18 : "The first two centimeters were excluded to neglect freshly deposited matter". We exclude this most of the times very fluffy material, as it possibly reflects just the most recent input to the sediments without any control over long-term deposition to the sediment record. We propose to add the statement : "as this material still passes through intense and rapid degradation".

P6 line 28. Not clear here the difference between TOC-MAR and OC (or TOC?) gross sedimentation rate.

We use same nomenclature as the paper cited "OC gross sedimentation rate" by Sobek et. al (2009). We define TOC-MAR on p5. l.7 as the organic carbon that is accumulated in the sediments while OC gross sedimentation rate is the deposition rate of OC onto the sediment surface (Sobek et. al 2009) often calculated by sediment trap data (see p.7 l.24-27 and Supplement Table S1). We propose to add a sentence to clarify this : "(deposition rate of OC onto the sediment surface)"

P9 line 22. Not clear what is meant by "accessibility of hypolimnetic O2 to the sediment surface"

We mean the O_2 flux to the sediments and will change the sentence to : "A closer look on the fluxes of reduced compounds produced by the deposited organic matter in the sediment, however, revealed that they as well depend on the concentration of O2 that the material was exposed to."(p.10 l.18-20).

Table 1. Units of Hypolimnetic volume is (Mm3) and not (m3).

We will change this to $10^6\,m^3$.

Sampling depth in Lake Baldegg 40m but 38m on table 2, Lake Geneva 40m but 45 on table 2.

We will make sure that sampling depths are consistent in the revised manuscript.

Fig S2. Concentrations in Lake Geneva at 310m are much lower throughout the year, varying between 2 and 5 mg/L (Barbier and Quetin 2016). To what year do these profiles correspond

We used the most recent data set we had from 2012 from CIPEL. We are now aware that apparently 2012 was one rare year in which O_2 levels became high in the deep basin. We will now use data from 2011 which more likely reflect the average O_2 concentrations in the deep basin and we will acknowledge CIPEL and INRA for the O_2 data of Lake Geneva.

Organic carbon mass accumulation rate regulates the flux of reduced substances from the sediments of deep lakes

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Abstract. The flux of reduced substances, such as methane and ammonium, from the sediment to the bottom water (F_{red}) is one of the major factors contributing to the consumption of oxygen in the hypolimnia of lakes and thus crucial for lake oxygen management. This study presents fluxes based on sediment porewater measurements from different water depths of five deep lakes of differing trophic states. In meso- to eutrophic lakes F_{red} was directly proportional to the total organic carbon mass accumulation rate (TOC-MAR) of the sediments. TOC-MAR and thus F_{red} in eutrophic lakes decreased systematically with increasing mean hypolimnion depth (z_H) suggesting that high oxygen concentrations in the deep waters of lakes were essential for the extent of organic matter mineralization leaving a smaller fraction for anaerobic degradation and thus formation of reduced compounds. Consequently, F_{red} was low in the 310 m deep meso-eutrophic Lake Geneva with high O_2 concentrations in the hypolimnion. By contrast, seasonal anoxic conditions enhanced F_{red} in the deep basin of oligotrophic Lake Aegeri. As TOC-MAR and z_H are based on more readily available data, these relationships allow estimating the areal O_2 consumption rate by reduced compounds from the sediments where no direct flux measurements are available.

1. Introduction

Hypolimnetic oxygen (O_2) depletion is a widespread phenomenon in productive lakes and reservoirs. Considerable work has been done to identify parameters responsible for hypolimnetic O_2 consumption (Livingstone and Imboden, 1996; Hutchinson, 1938; Cornett and Rigler, 1980), yet the key processes are still debated. Much to the irritation of lake managers, decreasing phosphorus (P) loads to lakes often did not result in a decrease of O_2 consumption in the hypolimnion, and O_2 consumption even increased in artificially aerated lakes (Müller et al., 2012a). An intuitive explanation for the lack of recovery of O_2 consumption is a delay caused by the mineralization of the large amount of organic carbon (OC) deposited in the sediments during hypertrophy, generating reduced species such as NH_4^+, CH_4, $Mn(II)$, $Fe(II)$ and $S(-II)$. By reacting with O_2 and other electron acceptors (directly or via microbial pathways), these reduced species contribute to the hypolimnetic O_2 consumption. As direct measurements of reduced substances are rare, several modeling approaches investigated the sediment oxygen demand related to the formation of reduced substances (Di Toro et al., 1990; Soetaert et al., 1996). Further, Matzinger et al. (2010) demonstrated that sediment deposits older than 10 years contributed only ~15% to the areal hypolimnetic mineralization rate (AHM), thus putting the magnitude and timescale of the "sediment memory effect" into perspective.

Müller et al. (2012a) proposed two key factors to be responsible for the AHM: (i) The diffusion controlled O_2 consumption by the mineralization of freshly settled OC at the sediment surface, and (ii) the O_2 consumed by the

oxidation of reduced substances diffusing from the sediment (F_{red}). The flux of O_2 from the bottom water to the sediment surface is a first order process with respect to the concentration of O_2 and hence lakes with a large hypolimnion volume can sustain a larger O_2 flux and increase the fraction of aerobically mineralized OC. As a consequence, AHM systematically increases with mean hypolimnion depth (z_H) of productive lakes. This relationship suggested a constant O_2 consumption rate of the sediments, which agreed with the few available estimations from direct sediment porewater measurements of reduced compounds. The fluxes of NH_4^+, CH_4, Fe(II), and Mn(II) from eutrophic lakes determined from porewater concentration profiles (summed up and expressed in O_2 consuming equivalents) were in a surprisingly narrow range of 0.36 ± 0.12 gO_2 m^{-2} d^{-1} (Müller et al., 2012a). This can be a substantial fraction of total AHM especially in lakes with a small hypolimnion volume. Matthews and Effler (2006) showed the importance of F_{red} for sediment O_2 demand in Onondaga Lake. Further, F_{red} was responsible for up to 42% and 86% of the total AHM in Pfäffikersee and Türlersee (Switzerland), respectively, where NH_4^+ and CH_4 fluxes represented up to 90% of F_{red}, while Fe(II) and Mn(II) fluxes played only a minor role (Matzinger et al., 2010).

Depending on the sedimentation regime and bottom water O_2 availability, F_{red} is expected to vary spatially. Carignan and Lean (1991) documented that porewater fluxes varied with lake depth and increased with increasing sedimentation rate in a mesotrophic but seasonally anoxic lake. They demonstrated the focusing of labile particulate OC as the cause for the depth dependence. In lakes Baldegg and Sempach, increasing Fe(II) and Mn(II) fluxes with lake depth were attributed to geochemical focusing (Urban et al., 1997; Schaller et al., 1997). In consequence, extrapolating measurements performed at the deepest sites of lakes to the entire hypolimnion area can significantly overestimate the contribution of reduced sediment compounds to AHM. Hence, the aim of this study is to systematically extend the knowledge of sediment flux measurements of reduced compounds and to identify a common driving factor of their creation. At least three sampling depths were selected in each of the five lakes investigated to gain information on the spatial distribution of fluxes of reduced substances. The combination of porewater sampling and on-site analysis with two portable capillary electrophoresis systems allowed a high sample throughput and the acquisition of an unprecedented dataset of porewater concentration profiles. Based on observations from 45 cores, this paper assesses the constraints of fluxes of reduced compounds (CH_4, NH_4^+, Mn(II), and Fe(II)) from the sediments of lakes with a range of trophic histories, discusses their spatial variabilities and the consequences for hypolimnetic O_2 consumption.

2. Materials and Methods

2.1. Study sites

Five lakes of different trophic states and depths were selected for the study (Table 1). Lake Baldegg (66 m depth) is located in an agricultural area dominated by pig farms. After 34 years of artificial aeration and mixing, it is still eutrophic with total phosphorus (TP) concentrations of $\sim$25 mgP m^{-3}. Lake Hallwil is the shallowest of the investigated lakes (48 m) and is presently recovering from its eutrophic past (TP $\sim$12 mgP m^{-3}) after 30 years of artificial aeration. Lake Aegeri is oligotrophic (TP $\sim$6 mgP m^{-3}) and located in a catchment dominated by pastures

and forests. Lake Geneva is the largest lake in Central Europe by volume. It is still meso-eutrophic (TP ~20 mgP m^{-3}) and the areal O_2 consumption rate is among the highest measured in Swiss lakes (Müller et al., 2012a; Schwefel et al., 2016). Lake Zug (197 m) is eutrophic, permanently stratified below ~100 m depth (meromictic) and has a TP value of ~30 mgP m^{-3} in the productive epilimnion. One set of cores for porewater analysis, CH_4 analysis and bulk sediment parameters was collected from the permanently oxic part (>4 mgO$_2$ L^{-1} throughout the year) at 62 m water depth.

2.2 Sediment sampling and porewater analysis

Sediment cores were retrieved with a Uwitec gravity corer equipped with a PVC tube (6.5 cm inner diameter, 60 cm length). The PVC tube has pre-drilled holes (Ø 2 mm) at 5 mm intervals. The holes were sealed with adhesive tape prior to sampling. Sediment cores were taken along a depth gradient (Table 1). Porewaters were sampled on site immediately after retrieval. 10-50 μL of sediment porewater were retrieved by punctuating the adhesive tape and horizontally inserting a MicroRhizon filter tube (1 mm diameter, 0.20 μm pore size; Rhizosphere Research Products, Wageningen, Netherlands). The sampling resolution was 5 mm for the first 5 cm of sediment, ≤ 1 cm between 5 cm and 10 cm of sediment, ≤ 2 cm between 10 cm and 20 cm of sediment and ≤ 3 cm below 20 cm of sediment. The porewater retrieval time was between 10 to 30 s and samples were immediately analyzed to minimize oxidation. Each porewater sample was analyzed once with two capillary electrophoresis devices each equipped with a capacitively coupled contactless conductivity detector (CE-C^{4}D) (calibrated for anions and cations) directly at the lake shore. Full separation of ions of interest (NH_4^+, Mn(II), Fe(II), SO_4^{2-}, NO_3^-, NO_2^-) was achieved within six minutes by applying a voltage of 15 kV and a current of 0.5 μA. The background electrolyte solution and all calibration standards were freshly prepared before sampling with UltraPure water (Merck) and the corresponding salts. All five-point calibrations were checked against a multi ion standard (Fluka), and standard deviations of all measurements were < 5%. The procedure is described in detail by Torres et al. (2013).

Methane samples were collected from additional sediment cores retrieved on the same day and location. Core liners had holes of 1.2 cm diameter pre-drilled staggered at 1 cm vertical intervals and covered with adhesive tape. Immediately after retrieval the cores were sampled in 1 cm steps from top to bottom by cutting the tape and inserting a plastic syringe where the tip was cut off. Two cm^3 of sediment were transferred into 125 ml serum flasks containing 2 ml of 7 M NaOH and capped with a septum stopper. Each CH_4 sample was analyzed three times in the headspace by gas chromatography (Agilent) using a 1010 Supelco Carboxene column with a standard deviation of 0.1 % to 1.3 %.

Additional sediment cores were extruded and sampled in 0.5 cm to 1 cm sections. Water content was calculated from the weight difference before and after freeze-drying, and the porosity estimated from the density and the respective TOC content (Och et al., 2012). Freeze-dried sediments were ground in an agate mortar and further analyzed for TOC/TN with an ElementAnalyzer Euro EA 3000 (Hekatech). Net sedimentation rates were determined based on the assumption of constant rate of supply with γ-ray measurements of ^{210}Pb and ^{137}Cs with a Canberra GeLi borehole detector and/or by varve counting which was possible in all cores except the cores from Lake Hallwil. The net sedimentation rates were further validated by the characteristic ^{137}Cs peaks of the Chernobyl fallout (1986) and the

bomb spike of 1963. As TOC content and net sedimentation rates were not determined from our sediment cores in Lake Geneva, literature data was used to calculate the total organic carbon mass accumulation rate (TOC-MAR, gC m^{-2} yr^{-1}). By comparing our coring sites to sites published by Span et al. (1990), Vernet et al. (1983) and Loizeau et al. (2012) we estimated an average net sediment accumulation rate of 1000 g m^{-2} yr^{-1} with a TOC content of 1.1 % resulting in TOC-MAR of 11 gC m^{-2} yr^{-1} for the deep basin. Although TOC content and net sedimentation can vary drastically due to turbidites and the inflow of the Rhone River, we deem this estimate to be representative for the deep undisturbed central basin of Lake Geneva.

2.3 Gross sedimentation

Sediment traps were deployed in Lakes Baldegg and Aegeri from March 2013 until the end of November 2014 to determine TOC gross sedimentation rates. In Lake Hallwil sediment traps were deployed from January 2014 to December 2014 (see Suppl. Information Table S1). The sediment trap material was collected biweekly. The traps consisted of two cylindrical PVC tubes with an inner diameter of 9.2 cm and were positioned at 15 m water depth and 1 m above the sediment surface. For the calculation of the gross sedimentation only data from the lower trap was used. The collected material was weighed, freeze-dried and analyzed for TOC and TN with the same methods as the sediment.

2.4 Calculation of the flux of reduced compounds

Porewater fluxes were calculated from vertical porewater concentration gradients with a one-dimensional reaction-transport model (Müller et al., 2003) that was adapted from Epping and Helder (1997) and extended from O_2 to other parameters. The fluxes (J) of reduced compounds (CH_4, NH_4^+, Fe(II), and Mn(II)), denoted in mmol m^{-2} d^{-1}, were multiplied with 32/1000 to be converted into equivalent O_2 fluxes (gO$_2$ m^{-2} d^{-1}) based on redox stoichiometry and summed up in F_{red} (Eq.1). S(-II) was considered negligible as we detected dissolved Fe(II) in all cores.

$$F_{red} = 2 * J_{CH4} + 2 * J_{NH4} + 0.5 * J_{Mn(II)} + 0.25 * J_{Fe(II)} \qquad (1)$$

F_{red} represents the total O_2 required per area to oxidize all reduced compounds released by the sediment (Matzinger et al., 2010). As total phosphorus concentration and hypolimnetic O_2 consumption rate did not change during the past years, sediment diagenetic processes are assumed to be in quasi steady state. Although seasonally varying deposition rates of OC and varying O_2 concentrations may alter Fe(II) and Mn(II) concentration gradients, the fluxes of NH_4^+ and CH_4 dominating F_{red} did not change systematically with the seasons.

2.5 Estimation of total organic carbon mass accumulation rates

Total organic carbon mass accumulation rate in the lake sediment (TOC-MAR, in gC m^{-2} yr^{-1}) at each coring site was calculated from the sedimentation rate (SR, in cm yr^{-1}), porosity (ϕ), dry density (ρ_{dry} in g cm^{-3}) and TOC (mg g^{-1}) for each 5 mm interval (Och et al., 2012) (Eq. 4). Porosity and dry density are calculated for each sampling interval individually (Eq. 1 and Eq. 3):

$$\phi = V_W / (V_w + V_s) \tag{1}$$

With V_w and V_s being the volumes of water and sediment, while the sediment volume can be calculated from its weight (W_s) and the dry density (Eq. 2):

$$V_s = W_s / \rho_{dry} \tag{2}$$

The dry density is estimated according to the empirical relationship between TOC content (in %) and density of geogenic sediments (Och et al., 2012)

$$dry\ density = -0.0523 * TOC + 2.65 \tag{3}$$

The TOC-MAR values were then averaged from 2 to 10 cm sediment depth. The first two centimeters were excluded to neglect freshly deposited matter as this material still passes through intense and rapid degradation. The lower TOC-MAR calculation depth of 10 cm was chosen to remain within the timeframe where steady state conditions can be assumed (Radbourne et al., 2017).

$$TOC - MAR = SR * \rho_{dry} * (1 - \phi) * 10000 * (TOC/1000) \tag{4}$$

3   Results and Discussion

3.1   Porewater concentration profiles and fluxes of reduced compounds

The porewater concentration profiles of the reduced compounds CH_4, NH_4^+, Fe(II), and Mn(II) measured at different depths in Lake Baldegg, Lake Aegeri, Lake Hallwil and Lake Geneva are presented in Figure 1, and for Lake Zug in Figure S1 (see Suppl. Information). The highest overall porewater concentrations occurred in Lake Baldegg (Figure 1a) and the lowest in Lake Geneva (Figure 1d) in spite of its high productivity. A distinct pattern of increasing porewater concentrations with increasing sampling depth was apparent in Lake Baldegg and to a lesser extent in Lake Aegeri (Figure 1a). Nitrate concentrations in the overlying water of the sediment core were on average 101 µmol L^{-1} in Lake Baldegg, 23 µmol L^{-1} in Lake Aegeri, 61 µmol L^{-1} in Lake Hallwil, 32 µmol L^{-1} in Lake Geneva and 20 µmol L^{-1} in Lake Zug and steeply declined to zero within the first cm of the sediment.

The trend of increasing ion concentrations with lake depth observed in the porewater was also reflected in the areal fluxes of the reduced compounds from the sediment to the lake bottom waters (Table 2). The fluxes were positive from the sediment to the bottom water in all lakes at all depths. Fluxes measured at the same locations on up to five different dates between March and October varied by 34% in Lake Baldegg and by 84% in Lake Aegeri for CH_4, and by 80% in Lake Baldegg and by 65% in Lake Aegeri for NH_4^+. The fluxes of Mn(II) (66% and 72%) and Fe(II) (46% and 88%) also showed a high variability. This temporal variation is likely due to local heterogeneity of the sediment and seasonal variations of both the supply of OC, e.g, algae blooms, and the O_2 concentration at the sediment-water interface. However, the relative importance of these driving factors could not be determined, and no clear seasonal pattern was detected.

A summary of all fluxes and F_{red} is given in Table 2. In Lake Baldegg the highest fluxes of CH_4, NH_4^+, and Fe(II) of all lakes, and a clear increase with sampling depth were observed. Fluxes at the deepest site agreed well with earlier measurements from dialysis samplers (Urban et al., 1997). In the oligotrophic Lake Aegeri fluxes of CH_4 and NH_4^+ were small at the shallow sites and similar to those observed in other oligotrophic lakes (Frenzel et al., 1990; Carignan et al., 1994), while at the deepest location considerably higher fluxes were measured for CH_4. Fluxes in Lake Hallwil did not show an overall increase with lake depth. In Lake Geneva, the smallest fluxes of CH_4, NH_4^+, and Fe(II) were observed in spite of its high productivity, without systematic variations with lake depth. NH_4^+ and CH_4 contributed 85% to 98% to the O_2 consuming capacity while Fe(II) and Mn(II) played only a minor role. Müller et al. (2012a) estimated F_{red} for a range of eutrophic lakes to be 0.36 ± 0.12 gO_2 m^{-2} d^{-1}, based on a relationship between hypolimnetic O_2 consumption rates and mean hypolimnion depths. F_{red} values observed at 24 m (0.28 gO_2 m^{-2} d^{-1}) and 40 m (0.34 gO_2 m^{-2} d^{-1}) depth in the eutrophic Lake Baldegg (see Table 2) matched the modeled value. F_{red} at the deepest site of Lake Baldegg (0.49 gO_2 m^{-2} d^{-1}) agreed with a previous observation of 0.55 gO_2 m^{-2} d^{-1}. Likewise in Lake Hallwil, F_{red} varied between 0.18 gO_2 m^{-2} d^{-1} and 0.25 gO_2 m^{-2} d^{-1}, matching earlier measurements of 0.28 gO_2 m^{-2} d^{-1} (Müller et al., 2012a). In Lake Aegeri, F_{red} was clearly higher at the deepest sampling site than at the shallower sites. At 34 m and 49 m water depth, F_{red} was 0.07 gO_2 m^{-2} d^{-1}, and thus typical for a deep oligotrophic lake. At 79 m, a markedly higher F_{red} of 0.24 gO_2 m^{-2} d^{-1} was observed. In eutrophic Lake Geneva, F_{red} varied between 0.02 and 0.09 gO_2 m^{-2} d^{-1}, which is surprisingly low for a productive lake. In summary, we did not observe a direct relationship between the trophic state of the lake and the fluxes of reduced substances.

Determination of sedimentation rates from core dating revealed increasing sediment deposition with increasing lake depth in Lake Baldegg and at the deepest site of Lake Aegeri. The sediment TOC content was around 3.4 % and varied only little between the different coring sites and lakes (see Table 2), except for Lake Geneva with an estimated 1.1% TOC. Consequently, mass accumulation rates varied substantially and increased with depth in Lake Baldegg and to a lesser extent in Lake Aegeri. We attribute this observation to sediment focusing, which has also been documented by Urban et al. (1997) for Lake Baldegg. Sediment focusing transports fine, freshly settled organic rich material from the shallower to the deeper parts of a lake and consequently increases TOC-MAR with lake depth (Lehman, 1975). Carignan and Lean (1991) documented that porewater fluxes increased with lake depth caused by the focusing of labile particulate OC into the deeper part of the lake. A study at oligotrophic Little Rock Lake also showed elevated NH_4^+ concentrations at the deepest site due to a greater supply of fine-grained organic particles caused by sediment focusing (Sherman et al., 1994). In eutrophic Lake Zug, Maerki et al. (2009) found that NH_4^+ fluxes increased proportionally with the sediment contents of TOC and total nitrogen (TN), indicating a link between fluxes of reduced substances and TOC-MAR. In Lakes Baldegg and Hallwil, geochemical focusing, caused by recurring redox-sensitive dissolution and precipitation of Mn and Fe phases, is an additional process that increases Fe(II) and Mn(II) concentrations with lake depth (Urban et al., 1997; Schaller and Wehrli, 1996).

Sediment focusing increased TOC-MAR by ~104% in the deepest part of Lake Baldegg and by ~43% in Lake Aegeri. Since F_{red} depends on the sedimentation regime and bottom water O_2 availability, this explains the spatial variability of F_{red} in these two lakes. No sediment focusing was observed in Lake Hallwil which is in agreement with a previous study by Bloesch and Uehlinger (1986). In consequence, extrapolating measurements performed at the

deepest sites of lakes to the entire lake area can significantly overestimate the average contribution of reduced sediment compounds to AHM in case sediment focusing is active.

3.2 F_{red} controlled by sediment TOC mass accumulation rate

All lakes investigated have a predominance of autochthonous OC input, implied by similar C/N ratios (7.0 – 9.9), a proxy for the origin of OC (see Table 2), and a permanently oxic hypolimnion (see Suppl. Information Fig S2). As a consequence, the burial efficiency of OC, defined as the ratio between TOC-MAR and OC gross sedimentation rate (deposition rate of OC onto the sediment surface) by Sobek et al. (2009) should be rather similar in these lakes. Based on gross TOC sedimentation data from sediment traps (see Suppl. Information Table S1) and TOC-MAR values (Table 2), burial efficiencies at the deepest sampling locations were calculated from sediment trap data of Lakes Baldegg (50 %), Hallwil (41 %) and Sempach (46 %). All values were close to the average value of 48% determined from 27 sediment cores from 11 lakes by Sobek et al. (2009). Consequently, a similar proportion of gross OC sedimentation is buried and contributes to the formation of F_{red} and TOC-MAR in all studied lakes. An exception is Lake Aegeri, with a surprisingly high burial efficiency of OC of 77 % calculated for the deepest site. However, this is caused by the exceptional bathymetry. The deepest site is located in a small trough with surrounding steep slopes predestined for sediment slides and remobilization of settled particles. The locally high ratio of sediment area to water volume presumably leads to the annual development of an anoxic deep water layer which increases OC burial, but is not representative for the whole lake.

As primary production and hypolimnetic O_2 concentrations did not change considerably during the last decade, the burial efficiency and thus TOC-MAR and F_{red} generation likely remained unchanged. Furthermore, porewater profiles do not capture the effects of rapid initial mineralization occurring within the top few millimeters of the sediment, but mirror the slower processes of anaerobic degradation of buried OC and F_{red}. Hence, in Figure 2 we related F_{red} to the corresponding TOC-MAR at each sampling location. Additional datasets from earlier measurements in various lakes were added to complement the relationship.

Figure 2 reveals two characteristic facts concerning the release of reduced compounds from lake sediments: (i) A distinct increase of F_{red} was observed when TOC-MAR exceeded ~10 gC m^{-2} yr^{-1}, (ii) F_{red} increased proportionately with TOC-MAR between 10 and 45 gC m^{-2} yr^{-1} up to ~0.50 gO$_2$ m^{-2} d^{-1} in all seasonally mixed lakes investigated. The highest F_{red} value was measured at the deepest point of Lake Baldegg with 0.49 gO$_2$ m^{-2} d^{-1} at a TOC-MAR of 45 gC m^{-2} yr^{-1}, despite much higher TOC-MAR in Rotsee. The mineralization of sediment OC appeared to be the main driver of F_{red} independent of the cause of TOC accumulation. The areal accumulation of TOC per time is controlled by gross sedimentation (which is related to primary production), O_2 concentration in the bottom water, biological factors like grazing and bioturbation, and physical parameters such as sediment focusing (Sobek et al., 2009). At low TOC-MAR, the total flux of reduced substances was very low (e.g Lakes Baikal, Erie and Superior, Figure 2), as only little carbon remained for anaerobic degradation, and the reduced substances diffusing up from deeper sediment strata were quantitatively oxidized in the upper sediment layers.

3.3 Factors limiting F_{red} and TOC-MAR

Given that all investigated lakes are seasonally mixed and have a permanently oxic hypolimnion, the likely driving factors for the positive relationship between F_{red} and TOC-MAR are (i) hypolimnetic O_2 concentrations, and (ii) the quality and quantity of OC. An influence of temperature and benthic production can be ruled out as all sampling stations were located in the cold hypolimnia well below the thermocline. Generally, high O_2 concentrations lead to a high fraction of aerobic OC mineralization and hence decrease of TOC-MAR as OC is decomposed by oxygenases and other reactive oxygen species (Maerki et al., 2006; Sobek et al., 2009; Stumm and Morgan, 1996). Furthermore, elevated hypolimnetic O_2 concentrations increase the oxidation of reduced compounds near or within the top sediment layer and thus increase the regeneration of alternative electron acceptors such as NO_3^- and SO_4^{2-} (Urban et al., 1997). In contrast, low O_2 concentrations or even temporally anoxic conditions increase OC burial and thus TOC-MAR and prompt the production of reduced compounds (Sobek et al., 2009).

Low TOC-MAR occurred in lakes with low primary production and low allochthonous input. In the oligotrophic Lakes Superior and Baikal, TOC-MAR was 4 and 7 gC m^{-2} yr^{-1} (see Suppl. Information Table S2), respectively, and the resulting F_{red} from the sediment was close to zero (Och et al., 2012; Klump et al., 1989; Remsen et al., 1989; Richardson and Nealson, 1989). In addition to low gross sedimentation of OC, the high sediment O_2 penetration depth (of around 1-3 cm) causes a long exposure time to oxic conditions and thus oxic mineralization of a large fraction of the deposit (Maerki et al., 2006; Martin et al., 1993; Li et al., 2012). In consequence, the TOC buried in lakes like Superior and Baikal is already highly mineralized and therefore does not generate significant amounts of reduced substances. However, low TOC-MAR were also observed in Lake Geneva. Although Lake Geneva is highly productive, its hypolimnetic O_2 concentration remained high throughout the year (see Suppl. Information Fig. S2) (Schwefel et al., 2016). Randlett et al. (2015) concluded that ~75% of the OC in Lake Geneva was mineralized aerobically at the sediment surface. Measurements performed by Schwefel et al. (2017) further confirmed that >96% of the OC in Lake Geneva is mineralized aerobically within the water column or at the sediment surface. As the buried OC only generated low F_{red} of 0.03 to 0.09 gO_2 m^{-2} d^{-1} (see Table 2), we concluded that the material was already recalcitrant. In contrast to the other lakes investigated, in Lake Geneva high porewater concentration and sediment penetration of SO_4^{2-} enhanced the degradation of OC and actively diminished F_{red} by oxidation of CH_4 and formation of Fe-sulfides. Norði et al. (2013) showed the efficiency of anaerobic CH_4 oxidation by SO_4^{2-} and a reactive Fe(III) pool which in turn reduced the flux of CH_4 out of the sediment. Sediment core measurements at 210 m and 240 m but in proximity to the Rhone River delta by Randlett et al. (2015) showed that at even higher TOC-MARs of 20 to 30 gC m^{-2} yr^{-1} (two to three times the rate estimated for the open lake), F_{red} values remained at similarly low values of 0.04 to 0.05 gO_2 m^{-2} d^{-1}. This case highlights the importance of OC quality, as refractory OC can be sequestered and offset TOC-MAR without a noticeable increase of F_{red}. Consequently, lakes with a higher input of land derived organic material should show a higher offset in TOC-MAR values as more recalcitrant OC is buried without a direct effect on F_{red}. While TOC-MAR values were similar at all three stations in Lake Aegeri, F_{red} peaked at the deepest point. In addition to a likely sediment focusing, a small anoxic bottom layer developed at the end of summer stratification at the deepest location (see Suppl. Information Fig. S2) due to the steep topography. This condition diminishes oxic mineralization of settled OC and thus supports the formation of higher F_{red}.

Under the assumptions that primary production even under ideal circumstances can generate only a limited amount of OC of around ~400 to 500 gC m^{-2} yr^{-1} (Wetzel, 2001) and that allochthonous, soil and land-plant derived OC is comparatively less accessible for mineralization, F_{red} is expected to converge at an upper bound even at high total TOC-MAR. As shallower lakes with a high primary production tend to become anoxic during the stratification period and thereby start accumulating reduced substances in the deepest part of the hypolimnion, F_{red} should not further increase as the concentration gradients between sediment and water would flatten as the oxic-anoxic interface moves from the sediment into the bottom water. The high F_{red} values encountered in Lake Baldegg (~0.49 gO$_2$ m^{-2} d^{-1}) supposedly represent an upper boundary of F_{red}, as it is an example of a highly eutrophic lake with an additional supply of OC to the deepest part by sediment focusing while only retaining an oxic hypolimnion due to artificial aeration. At the highest TOC-MAR value of ~170 gC m^{-2} yr^{-1} measured in the seasonally anoxic Rotsee (RO), F_{red} remained at 0.46 gO$_2$ m^{-2} d^{-1} (measured after lake mixing in the oxic hypolimnion), showing no further increase of F_{red}, while measurements performed at the end of summer stagnation and an anoxic hypolimnion revealed a F_{red} value of 0.26 gO$_2$ m^{-2} d^{-1}. However, whether F_{red} consistently levels off at high TOC-MAR remains to be verified by measurements in additional eutrophic lakes with an oxic hypolimnion and high TOC-MAR.

3.4 Relationship between F_{red} and mean hypolimnion depth

The increasing fraction of oxically mineralized OC with increasing O$_2$ availability in eutrophic lakes is further supported by a systematic decrease of F_{red} with increasing mean hypolimnion depth (z_H) in productive lakes, shown in Figure 3. During the stratified period, the hypolimnetic O$_2$ reservoir in eutrophic lakes with a small z_H is quickly exhausted, enforcing a higher OC burial rate, increased anaerobic mineralization, and thus the formation of reduced substances e.g. in Rotsee, Türlersee and Pfäffikersee. In these lakes F_{red} becomes the dominant fraction of AHM with values of ~0.40 gO$_2$ m^{-2} d^{-1}. In the deep Lake Geneva, the hypolimnetic O$_2$ inventory increases with z_H, and the lakes' resilience to O$_2$ depletion rises. Consequently, more O$_2$ is available for aerobic remineralization of OC, and hence less or more degraded OC is buried. Hence F_{red} diminishes with increasing z_H. Coherently, very deep eutrophic lakes such as Lake Geneva are well protected from anoxia. Lake Baldegg deviates from this general correlation in Figure 3 due to the high sediment focusing, which caused the sedimentation rate to increase by a factor of 1.9 compared to the shallower sites. Likewise, sediment focusing might increase F_{red} in other lakes. Yet it is unclear to what extent sediment focusing increases F_{red} and TOC-MAR, for example, in Lake Sempach (Urban et al., 1997). These findings complement and extend the observation presented in Müller et al. (2012a) that AHM of fully productive lakes increased linearly with their mean hypolimnion depth if $z_H <$ ~25 m, with a similar contribution of reduced compounds from the sediments of all lakes. A closer look on the fluxes of reduced compounds produced by the deposited organic matter in the sediment, however, revealed that they as well depend on the concentration of O$_2$ that the material was exposed to.

4 Conclusion

We demonstrate that the areal oxygen consumption in lakes caused by reduced compounds diffusing from the sediment, F_{red}, is strongly related to the local mass accumulation rate of OC (Figure 2). In fully productive eutrophic

lakes, the flux of reduced compounds, F_{red}, declines with increasing mean hypolimnion depth (z_H) due to the higher O_2 bottom water concentration and thus increasing exposition time of settled OC to O_2 (Figure 3). Hence, in these lakes, z_H can serve as a proxy for F_{red}. These observations indicate that F_{red} from the sediment is constrained mainly by the deposition rate and quality of OC, O_2 availability to the sediment surface and lake bathymetry (i.e. the occurrence of sediment focusing. The sediment O_2 demand, a major sink for O_2 in the hypolimnion, can now be estimated for a broad range of lakes with a permanently oxic hypolimnion without elaborate O_2 measurements at the sediment-water interface based on the relationships between F_{red} and TOC-MAR and between F_{red} and z_H, which are more commonly available than porewater measurements.

5   Data Availability Statement

The data will be made available over Figshare.com

6   Appendices

Table S1 summarizes parameters used for OC burial efficiency rate calculations e.g. TOC-MAR values and benthic OC gross sedimentation. Table S2 sums up information about F_{red} and TOC-MAR values of lakes taken or calculated from literature. Figure S1 shows the porewater concentrations of CH_4, NH_4^+, Fe(II) and Mn(II) in the sediment of Lake Zug at 62 m water depth, Figure S2 depicts the O_2 concentrations throughout one year in five different lakes at the core sampling depths.

Author contribution statement

MS, AW, BW and BM designed the study. TS conducted porewater measurements and analyzed the sediment cores and wrote the manuscript. RS performed O_2 microprofiles. All authors contributed to the writing of the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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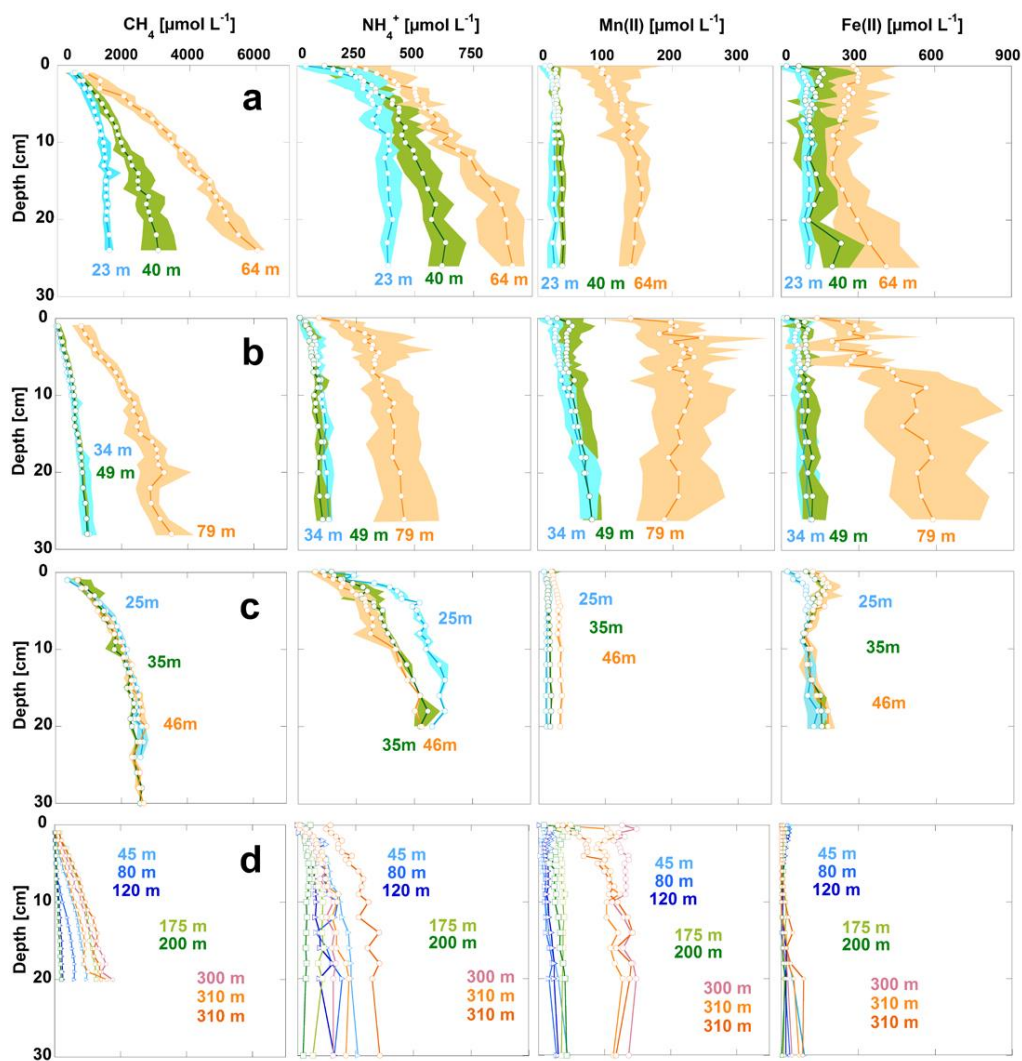Wetzel, R.: Limnology, Academic Press, 2001.

Figure 1. Porewater concentration profiles of NH_4^+, CH_4, Mn(II), and Fe(II) from a) Lake Baldegg, b) Lake Aegeri, c) Lake Hallwil, and d) Lake Geneva. Bold lines are averaged values of up to five measurements while the areas of corresponding colors show the range of minimal and maximal values. Coring sites of Lake Geneva (d) were sampled only once.
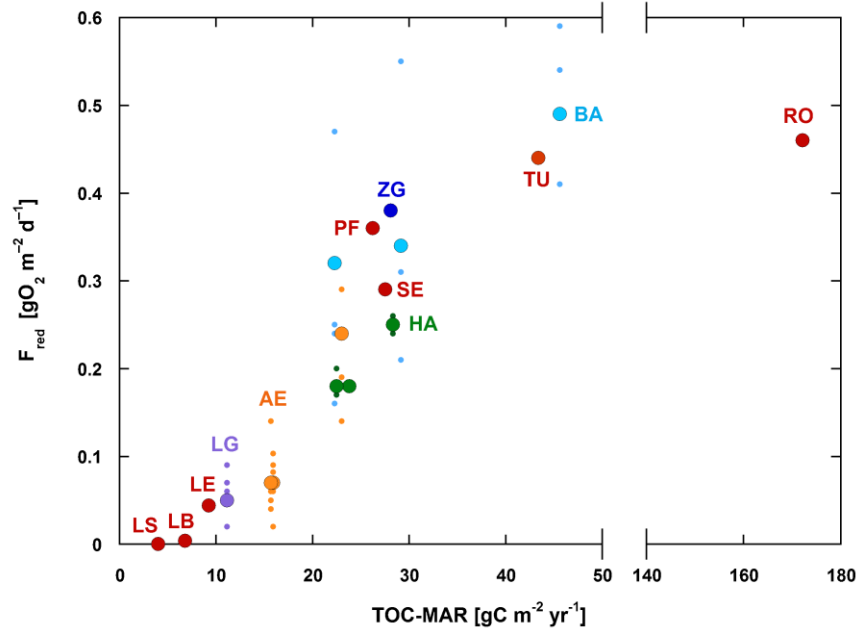
Figure 2. F_{red} of 11 different lakes plotted against the total organic carbon mass accumulation rate (TOC-MAR). Values for Lakes Baldegg (BA), Hallwil (HA) and Aegeri (AE) were averaged from up to five measurements (big circles), those for Lake Zug (ZG) were calculated from a single core at 62 m water depth. Small circles show each individual F_{red} result at the respective sampling location. The variations of F_{red} in Lake Geneva show only the variations due to sampling depths as all cores were collected in summer. Red marks were calculated from single core literature data (Lake Baikal (LB), Och et al. (2012); Lake Sempach (SE), Müller et al. (2012b); Rotsee (RO), Naeher et al. (2012); Pfäffikersee (PF, unpublished); and Türlersee (TU, unpublished)). TOC-MAR from Lake Geneva (LG) are based on sedimentation rate estimates from the literature (Vernet et al., 1983; Loizeau et al., 2012; Span et al., 1990). TOC-MAR and F_{red} values from Lake Erie (LE) were extracted from Matisoff et al. (1977), Adams et al. (1982) and Smith and Matisoff (2008). Values for Lake Superior (LS) were compiled from Klump et al. (1989), Remsen et al. (1989), Richardson and Nealson (1989), Heinen and McManus (2004) and Li et al. (2012).
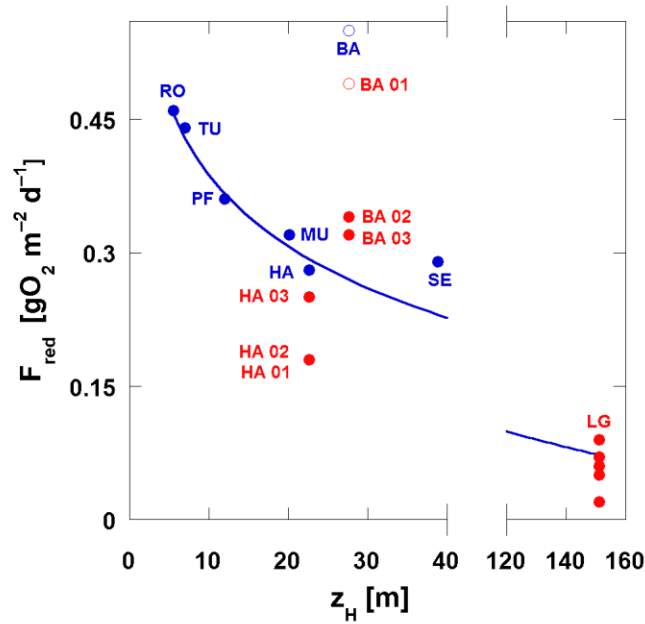
Figure 3. Average fluxes of reduced compounds from the sediments of eight meso- to eutrophic lakes decrease systematically with mean hypolimnion depth (z_H), except for sediments sampled at the deepest sites of lakes with pronounced sediment focusing (BA, BA 01, open circles). F_{red} values of Lake Baldegg (BA01 to 03) show a significant increase with sampling depth due to strong sediment focusing. Blue circles indicate data for Rotsee (RO), Türlersee (TU), Pfäffikersee (PF), Lake Murten (MU), and Lake Sempach (SE), taken from Müller et al. (2012a) while red circles show data of the current study. Meromictic Lake Zug is not shown. The blue line is used for eye guidance.

Table 1. Lake characteristics, sampling depths and dates. The mean hypolimnion depth (z_H) is defined as the hypolimnetic volume divided by the hypolimnetic area below 15 m water depth.

Lake	Tropic status	Hypolimnion surface area, (km^2)	Hypolimnion volume (10^6 m^3)	z_H (m)	Max. depth (m)	Sampling depths (m)	Sampling time
Lake Baldegg	eutrophic	4.53	125	27.6	66	23, 40, 64	March 2013, May 2013, August 2013, October 2013, March 2014,
Lake Aegeri	oligotrophic	6.64	283	42.6	81	34, 49,79	March 2013, May 2013, August 2013, October 2013, March 2014,
Lake Hallwil	Mesotrophic recovering	8.58	194	22.6	48	25, 35, 46	April 2014, August 2014
Lake Zug	eutrophic - meromictic	34.5	2660	77.1	197	62	Mai 2016
Lake Geneva	Meso- eutrophic	534	80800	151	310	45**, 80*, 120**, 175*, 200*, 300*, 310* and **	*July 2014, ** July 2015

Table 2. Results from sediment and porewater analyses. Porewater fluxes are averaged over all flux measurements of each individual species. Standard deviations (±) are based on all measurements. TOC was averaged from 2 to 10 cm sediment depth. TOC and net sedimentation from Lake Geneva were not determined (n.d). Lake Baldegg (BA), Lake Aegeri (AE), Lake Hallwil (HA), Lake Zug (ZG) and Lake Geneva (LG).

Core	Depth (m)	SR (mm yr^{-1})	TOC (%)	C/N ratio	J_{NH4}	J_{CH4}	$J_{Fe(II)}$	$J_{Mn(II)}$	F_{red} (gO$_2$ m^{-2}d^{-1})	TOC-MAR (gC m^{-2} yr^{-1})	No. Cores
					(mmol m^{-2} d^{-1})						
BA 03	23	1.75	2.70	7.5	2.04±1.62	2.16±0.74	0.34±0.14	0.05±0.03	0.28±0.11	22.3	5
BA 02	40	2.63	2.63	7.0	2.19±1.34	2.79±0.84	0.40±0.08	0.07±0.03	0.34±0.14	29.1	5
BA 01	64	3.32	3.42	7.5	2.84±1.23	4.24±0.57	1.00±0.39	0.22±0.11	0.49±0.09	45.6	5
AE 03	34	1.43	3.49	8.1	0.45±0.25	0.62±0.42	0.33±0.29	0.08±0.04	0.07±0.04	16.0	5
AE 02	49	1.37	3.47	7.6	0.50±0.21	0.49±0.41	0.34±0.21	0.18±0.13	0.07±0.03	16.3	5
AE 01	79	1.91	3.43	7.9	1.44±0.94	2.06±0.99	0.69±0.32	0.41±0.17	0.26±0.08	22.8	5
HA 03	25	2.00	3.46	9.9	1.58	2.26	0.28	0.03	0.25	28.3	2
HA 02	35	1.93	3.42	9.5	1.18	1.64	0.40	0.04	0.18	23.8	2
HA 01	46	1.95	3.41	9.9	0.98	1.74	0.53	0.05	0.18	22.5	2
ZG	62	2.80	3.99	7.6	2.80	3.11	0.24	0.03	0.38	28.1	1
LG 08	45	n.d	n.d	n.d	0.26	0.45	0.18	0.01	0.05	n.d	1
LG 07	80	n.d	n.d	n.d	0.42	0.41	0.14	0.03	0.05	n.d	1
LG 06	120	n.d	n.d	n.d	0.16	0.11	0.16	0.05	0.02	n.d	1
LG 05	175	n.d	n.d	n.d	0.15	0.87	0.03	0.05	0.07	n.d	1
LG 04	200	n.d	n.d	n.d	0.13	0.08	0.11	0.04	0.02	n.d	1
LG 03	300	n.d	n.d	n.d	0.21	0.61	0.00	0.15	0.05	n.d	1
LG 02	310	n.d	n.d	n.d	0.30	0.54	0.04	0.21	0.06	n.d	1
LG 01	310	n.d	n.d	n.d	0.52	0.79	0.12	0.16	0.09	n.d	1