

Hypolimnetic Oxygen Depletion in Eutrophic Lakes

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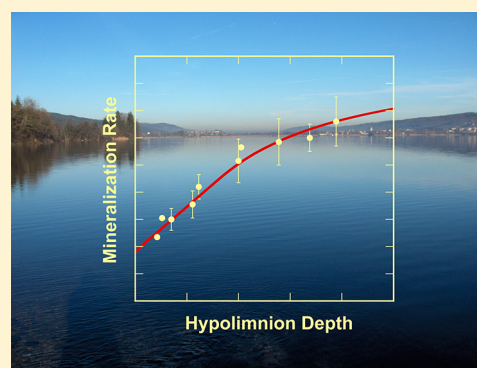
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Supporting Information

ABSTRACT: The oxygen-consuming processes in the hypolimnia of freshwater lakes leading to deep-water anoxia are still not well understood, thereby constraining suitable management concepts. This study presents data obtained from 11 eutrophic lakes and suggests a model describing the consumption of dissolved oxygen (O_2) in the hypolimnia of eutrophic lakes as a result of only two fundamental processes: O_2 is consumed (i) by settled organic material at the sediment surface and (ii) by reduced substances diffusing from the sediment. Apart from a lake's productivity, its benthic O_2 consumption depends on the O_2 concentration in the water overlying the sediment and the molecular O_2 diffusion to the sediment. On the basis of observational evidence of long-term monitoring data from 11 eutrophic lakes, we found that the areal hypolimnetic mineralization rate ranging from 0.47 to 1.31 g of O_2 m⁻² d⁻¹ (average 0.90 ± 0.30) is a function of (i) a benthic flux of reduced substances (0.37 ± 0.12 g of O_2 m⁻² d⁻¹) and (ii) an O_2 consumption which linearly increases with the mean hypolimnion thickness (z_H) up to ~25 m. This model has important implications for predicting and interpreting the response of lakes and reservoirs to restoration measures.



INTRODUCTION

Depletion of dissolved oxygen (O_2) in the hypolimnia of lakes during stratification and its deleterious effect on fish stocks have been observed and analyzed for more than 100 years. Issues with water quality related to O_2 depletion from lake hypolimnia during the stratified productive season led to increased lake and reservoir management during the 1960s and 1970s.¹ As biologically available phosphorus (BAP) was recognized as the driving force for primary productivity, management efforts focused primarily on reducing phosphorus (P) loads to lakes.^{1,2} As a result, P concentrations decreased in many lakes since the mid-1970s and early 1980s, creating a success story in water management.³

It was soon recognized, however, that the link between BAP and hypolimnetic O_2 consumption was more complex than initially realized. On one hand, internal lake measures such as hypolimnetic oxygenation through artificial aeration/oxygenation, with the aim of preventing the release of phosphate from the reduced sediment, did not show the expected success.⁴ On the other hand, it was puzzling to observe that, in some artificially oxygenated lakes, hypolimnetic O_2 depletion remained unaffected or even increased while the reduction of the BAP load lowered the in-lake BAP concentration from >500 to <30 mg of P m⁻³.⁵

The Vollenweider model,¹ which facilitated understanding of production-relevant BAP fluxes, had a tremendous impact on

lake management. However, we still struggle to conceptually comprehend the processes controlling O_2 consumption and subsequent depletion in the water column. Hutchinson⁶ introduced the “apparent oxygen deficit” per area of the hypolimnion, later deemed as “areal hypolimnetic oxygen demand (AHOD)”, to quantify hypolimnetic O_2 depletion and complemented the concept by defining the “real oxygen deficit”. Building on this work, Matzinger et al.⁷ defined a comprehensive areal hypolimnetic mineralization (AHM) rate and applied it to the analysis of long-term data series for two eutrophic lakes with periodically anoxic hypolimnia. In agreement with Hutchinson’s real oxygen deficit, AHM is equal to AHOD in the presence of O_2 but also includes accumulated reduced substances (e.g., methane (CH_4) and ammonium (NH_4^+)) released from the sediment after hypolimnetic O_2 depletion. Hypolimnetic O_2 -consumption data were then combined with porewater measurements to isolate the fractions of AHM resulting from (i) the mineralization of freshly settled organic matter (OM) and (ii) reduced substances released from the anoxic sediment.

A number of empirical models have been developed that relate hypolimnetic O_2 consumption to various physical and environ-

Received: April 10, 2012

Revised: July 23, 2012

Accepted: August 7, 2012

Published: August 7, 2012

Table 1. Physical and Hydrological Characteristics and Areal Hypolimnetic Oxygen Consumption Rates (AHM) Calculated from Monitoring Data of 11 Eutrophic Lakes Included in the Study^a

lake	surface area, km ²	lake volume, 10 ⁶ m ³	max depth, m	A _H , km ²	V _H , 10 ⁶ m ³	z _H , m	AHM, g of O ₂ m ⁻² d ⁻¹	std dev, %	no. of years monitored	measures, remarks	ref
Lauerzersee	3.07	23	13	2.31	9.8	4.2	0.47		2		
Rotsee	0.47	3.81	16	0.33	1.81	5.5	0.61		1		37
Türlensee	0.5	6.5	22	0.33	2.3	7.0	0.60	13	23	destrat during winter	7
Greifensee	8.45	149	32	6.44	74.3	11.5	0.71	13	18		38
Pfäffikersee	3.03	57.1	35	2.45	29.5	12.0	0.84	10	22	destrat during winter	7
Murtensee	22.8	533	46	16.9	339	20.1	1.03	15	23		
Hallwilersee	9.95	286	48	8.58	194	22.6	1.13 (1.39)	1 (15)	3 (24)	oxygenated/destrat	39
Baldeggersee	5.22	174	66	4.53	125	27.6	1.17 (1.67)	15 (13)	4 (29)	oxygenated/destrat	39
Lac d'Annecy	24.5	1030	65	23.3	787	33.8	1.20	8	5	meso-eutrophic	40
Sempachersee	14.1	640	86	13.0	505	38.8	1.32 (1.46)	14 (17)	16 (28)	destrat during winter	39
Lake Geneva	582	89,100	310	534	80,800	151	1.41	20	10	formerly eutrophic	41

^aO₂ was depleted at the end of the stratification period in all lakes. A_H and V_H indicate the area and volume of the hypolimnia, respectively; z_H = V_H/A_H is the mean hypolimnion thickness. AHM values for Baldeggersee, Hallwilersee, and Sempachersee are for the period prior to aeration; values during aeration are given in parentheses. If observations from several years were available, average AHM values were obtained by calculating the arithmetic mean of annual observations.

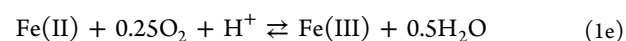
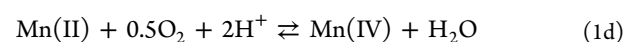
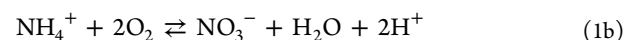
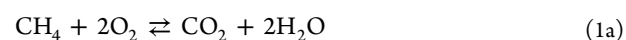
mental parameters.^{8–10} Considerable work has been done by Cornett and Rigler,^{11,12} who established an empirical relationship explaining AHOD with three primary parameters (P retention, mean hypolimnetic summer temperature, and mean hypolimnion thickness, z_H). Surprisingly, z_H alone explained a significant fraction of AHOD variation. This led to the interpretation that benthic O₂ consumption was of limited importance and AHOD increased with increasing z_H mainly because settling organic matter had more time to decompose in the water column of deeper lakes.

More recently, specific focus has been placed on applying empirical models to lake and reservoir management and the design of hypolimnetic oxygenation systems.^{13–15} The general applicability of many of the existing models, however, is often limited due to the lack of required limnological data (e.g., primary production, net sedimentation of P, sediment oxygen demand).¹⁶ Thus, lake managers are looking for a generally applicable model predicting the hypolimnetic O₂ demand with a reasonable accuracy without requiring extensive lake-specific data sets. This study introduces such a model, describing hypolimnetic O₂ depletion in eutrophic lakes solely as a function of z_H. The model is applicable for lakes with excessive sediment oxygen demand, i.e., with virtually no O₂ in the sediment. The cause for the sediment oxygen demand can be either present or past lake eutrophication.

MATERIALS AND METHODS

Study Sites. The study is based on data from one French and ten Swiss eutrophic lakes briefly characterized in Table 1 and nine mesotrophic and oligotrophic Swiss lakes presented in Table SI-1, Supporting Information. Lake Geneva is a formerly eutrophic lake that has turned mesotrophic over the past decade but with still organic-rich sediments. All eutrophic lakes sustain substantial hypolimnetic O₂ depletion toward the end of the stratification period, especially those not artificially aerated. For details on the technical restoration measures, we refer to the indicated references.

Estimation of Areal Hypolimnetic Mineralization Rates. Conceptually, AHM not only quantifies O₂ consumption induced by the mineralization of recently settled organic material but also characterizes the flux of reduced substances (F_{red}) diffusing from deeper sediment layers toward the sediment surface expressed as the O₂ equivalent necessary for their oxidation as indicated in the following equations:



For artificially aerated lakes (Sempachersee, Baldeggersee, and Hallwilersee), AHM rates were determined both during periods of aeration and prior to aeration. Detailed quantification of O₂ introduced by aeration was available from the Cantonal Bureaus for the Environment of Aarau and Lucerne and was included in the AHM. The mean hypolimnion thickness z_H was estimated from the hypolimnion volume derived from bathymetric maps divided by the area at the estimated average top of the hypolimnion at 10 m depth (Table 1). The mean epilimnion thickness as estimated from temperature and O₂ profiles increased typically during the stratified season from ~7.5 to ~10 m, corresponding to the spatial resolution of chemical samples, and was consequently difficult to determine accurately; therefore, we considered a mean epilimnion thickness of 10 m to be most appropriate in view of the seasonal dynamics as well as for the sake of simplicity and universal versatility of the model (four examples are given in the Supporting Information, Figure SI-1). For the two shallowest lakes, Lauerzersee and Rotsee, the mean epilimnion thickness was estimated on the basis of temperature and O₂ depletion profiles as 5 and 6 m, respectively.

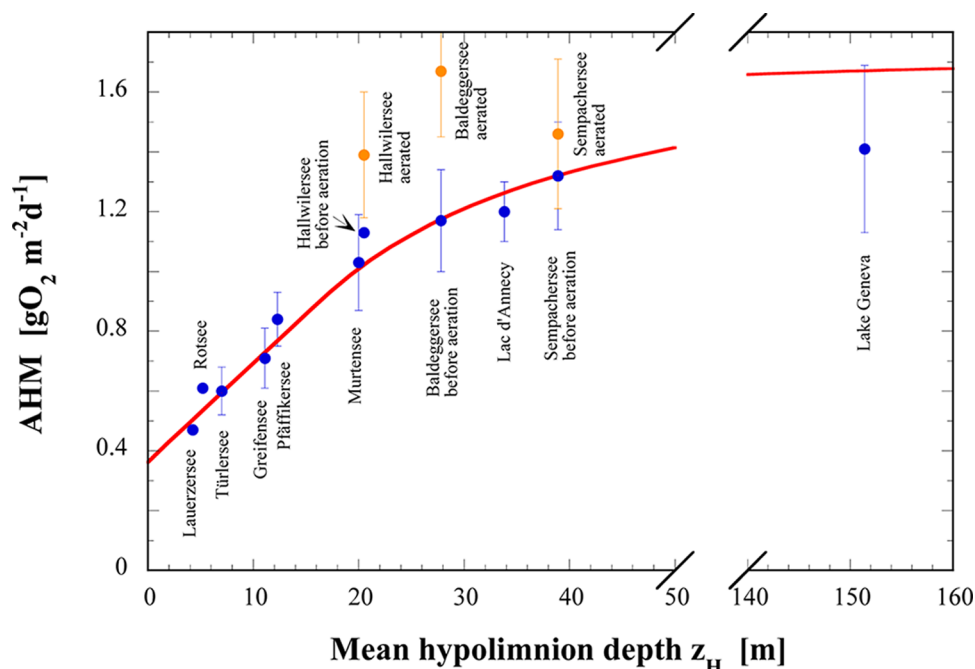


Figure 1. AHM rates of 10 eutrophic lakes and the formerly eutrophic Lake Geneva, detailed in Table 1, plotted against the average hypolimnion thickness z_H . Aerated lakes are marked by orange dots. The red line shows the model fit defined by eq 6 using $F_{\text{red}} = 0.36 \text{ g m}^{-2} \text{ d}^{-1}$, an initial (spring) O_2 concentration $C(0) = 11 \text{ g m}^{-3}$, and a diffusive boundary layer thickness $\delta = 0.82 \text{ mm}$ adjusted by least-squares fitting. Indicated values and error bars represent arithmetic means over multiple years and standard deviation, respectively.

Water Chemical Analyses. O_2 concentrations were determined according to Carpenter¹⁷ in water samples collected in vertical profiles at the lake's deepest sites. Concentrations of NH_4^+ and NO_2^- were evaluated by photometric standard procedures.¹⁸ Dissolved CH_4 was determined as described in the following section.

Sediment Analyses, Porewater Analyses, and Sediment-to-Water Flux Estimates. Sediment cores were collected using a Uwitec corer (www.uwitec.at) equipped with PVC tubes 6.5 cm in diameter and 60 cm in length. For CH_4 sampling, 12 mm diameter holes were drilled in 10 mm increments into the tube in an offset pattern and sealed with tape. Immediately after retrieval of the cores, the overlying water was transferred bubble-free to a 100 mL serum bottle containing a few pellets of solid NaOH to stop bacterial activity, and the bottle was sealed with a septum stopper. The tape covering each hole was then cut open, and a subcore of 2 cm^3 volume was sampled horizontally using a 2 mL syringe with a trimmed tip. The subcore was then transferred into a 25 mL serum bottle with 4 mL of 2.5% NaOH and sealed with a septum stopper. The entire sampling procedure was accomplished within ~ 10 min after retrieval of the core. CH_4 was measured in the headspace of the subcore sample by gas chromatography (Agilent) using a Supelco Carboxene 1010 column.

Sediment porewater (3–6 mL) was extracted from the cores by gentle vacuum filtration of 5 mm thick subslices using $0.45 \mu\text{m}$ cellulose acetate membrane filters (Sartorius 11106-85, Germany). Anions and cations (including Mn(II)) were analyzed with ion chromatography (Metrohm, Switzerland). NH_4^+ and S(-II) were determined photometrically according to standard methods.¹⁸ Filterable Fe was measured from acidified samples (HNO_3 suprapure) by inductively coupled plasma optical emission spectroscopy (ICP-OES; Spectro-Ciros). The remaining sediment was freeze-dried, ground in an agate mortar, and analyzed for total carbon and total nitrogen using an

ElementalAnalyzer Euro EA 3000 (Hekatech) and for total inorganic carbon using a Coulometer (CM5015 UIC).

On the basis of these data and following refs 7 and 19, fluxes of dissolved compounds across the sediment–water interface were estimated using a one-dimensional model to equate diffusive transport to the production rate on a local scale.

RESULTS AND DISCUSSION

AHM Rates in Hypolimnia of Eutrophic Lakes. In spite of the high diversity in size and depth of the lakes included in the study, AHM values remained within a narrow range of $0.90 \pm 0.30 \text{ g of O}_2 \text{ m}^{-2} \text{ d}^{-1}$ with a low lake-specific interannual variability of only $\sim 12\%$ (Table 1). Rates of AHM plotted as a function of z_H (Figure 1) result in a striking relationship between AHM and z_H ; i.e., AHM increases with z_H almost linearly up to $\sim 25 \text{ m}$ and then levels off with increasing z_H . The linear fit to the seven lakes of shallowest hypolimnia in Figure 1 results in an intercept ($z_H = 0$) of $0.36 \text{ g of O}_2 \text{ m}^{-2} \text{ d}^{-1}$. Two major processes derived from the model presented below explain this behavior.

Model for Hypolimnetic O_2 Consumption in Eutrophic Lakes. Figure 1 shows that AHM attains a positive value when z_H approaches zero. This indicates a constant contribution of the sediment to AHM, which is quantified as the (areal) flux of reduced substances to the hypolimnion water. The second process causes AHM to steadily increase with increasing z_H up to $\sim 25 \text{ m}$ and level off for thicker z_H . The O_2 mass balance in a hypolimnetic water volume ΔV bordered by a sediment surface ΔA is expressed by

$$\Delta V \frac{dC}{dt} = -\Delta A F_{\text{red}} - \Delta A \frac{D_{\text{O}_2}}{\delta} C(t) \quad \text{for } C(t) \geq 0 \text{ g m}^{-3} \quad (2)$$

$$\Delta V \frac{dC}{dt} = -\Delta A F_{\text{red}} \quad \text{for } C(t) < 0 \text{ g m}^{-3} \quad (3)$$

where dC/dt ($\text{g m}^{-3} \text{ d}^{-1}$) is the rate of change in O_2 concentration ($C(t)$, g m^{-3}), which is governed by (i) F_{red} , the diffusive benthic flux of reduced substances into the water across the area ΔA ($\text{g of O}_2 \text{ m}^{-2} \text{ d}^{-1}$), and (ii) molecular O_2 diffusion through the diffusive boundary layer (DBL) to the sediment. D_{O_2} is the molecular O_2 diffusion coefficient ($\text{m}^2 \text{ d}^{-1}$), and δ is the thickness of the DBL (m). Equations 4 and 5, obtained by integrating eqs 2 and 3 and performing a mass balance over the entire hypolimnion volume, $V_H = A_H z_H$ (m^3), express dC/dt as a function of time t . Under the assumption of a completely mixed hypolimnion and constant parameters F_{red} , D_{O_2} , and δ , the O_2 balance in V_H thus reads

$$\frac{dC}{dt} = -\frac{1}{z_H} F_{\text{red}} - \frac{D_{\text{O}_2}}{\delta z_H} C(t) \quad \text{for } C(t) \geq 0 \text{ g m}^{-3} \quad (4)$$

$$\frac{dC}{dt} = -\frac{1}{z_H} F_{\text{red}} \quad \text{for } C(t) < 0 \text{ g m}^{-3} \quad (5)$$

Solutions for the differential eqs 4 and 5 are given in the Supporting Information (eqs 4a and 5a).

The volume-specific rate, dC/dt , defined in eqs 4 and 5, can be transformed to a seasonal AHM by integration over the entire hypolimnion of average thickness z_H and over the stratification period of $\Delta t = 200$ d (April to October)

$$\text{AHM} = F_{\text{red}} + \frac{D_{\text{O}_2}}{\delta \Delta t} \int_{\text{for } C > 0}^{0-200\text{d}} C(t) dt \quad (6)$$

whereas the integration is applied only during periods with $[\text{O}_2] > 0 \text{ g m}^{-3}$, as O_2 can only be consumed as long as it is available. As the diffusive flux of O_2 to the sediment (second term in right-hand side of eq 6) is proportional to $C(t)$, AHM depends on the temporal development of C . In other words, AHM decreases as a function of O_2 diffusion to the sediment surface (first-order kinetic reaction) during the course of summer stratification, while F_{red} , which depends on the slowly changing supply of OM in the anaerobic sediment (zero-order reaction), remains unaffected.

In cases where other oxidants in addition to O_2 , such as NO_3^- , SO_4^{2-} , or iron(III)/manganese(IV) oxides, oxidize reduced substances in the hypolimnion, the definition of AHM can be extended to include the respective oxidants expressed in their O_2 equivalents. Including NO_3^- in the AHM estimation of the 11 eutrophic lakes presented in Figure 1 results in increases in AHM by 0–6% with the exception of Greifensee, where AHM is 17% higher if denitrification is considered (Table SI-2, Supporting Information).

Figure 1 shows that eq 6 predicts observed AHM rates of eutrophic lakes well over a large range of z_H by setting $F_{\text{red}} = 0.36 \text{ g of O}_2 \text{ m}^{-2} \text{ d}^{-1}$, the initial O_2 concentration in the hypolimnion as 11 g m^{-3} , and the thickness of the DBL $\delta = 0.82 \text{ mm}$. This least-squares-fitted value for δ is within a broader range of average δ measurements obtained during previous studies of O_2 fluxes across the sediment–water interface in Lake Alpnach as determined with in situ O_2 microsensors and bottom water current measurements (0.16 – 0.84 mm^{20} and 1 – 2 mm^{21}).

As shown in Figure 1, the shallower the hypolimnion, the more F_{red} contributes to the total AHM. In eutrophic lakes, gross primary production and hence the annual sediment load of OM are likely relatively independent of z_H ; thus, this implies that in

lakes with deep hypolimnia most of the settled OM is oxidized with O_2 as an electron acceptor during summer whereas in shallow hypolimnia this terminal oxidation mainly occurs during subsequent winter overturn. For the applicability of the model, it is not essential that the lake is presently eutrophic but that there is enough organic matter in the sediment so that the sediment surface is virtually free of O_2 . Consequently, O_2 consumption by the sediment is controlled by the molecular flux through the diffusive boundary layer from the hypolimnion into the sediment. As a result of the anoxic sediment, the flux of reduced substances from the sediment becomes a relevant part of the O_2 depletion in the hypolimnion. This is supported by the example of Lake Geneva (Figure 1), a formerly eutrophic lake that has partly recovered but still has an organic-rich sediment with a high O_2 consumption.

The model predicts that at a characteristic hypolimnion thickness the available O_2 is depleted during the stratified period. Figure 2 shows the seasonal decrease of $C(t)$ for three arbitrarily

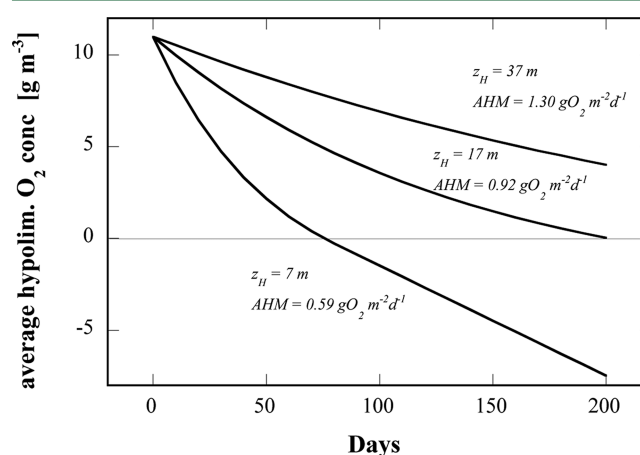


Figure 2. Decreasing O_2 concentrations in three hypolimnia with different values of z_H as calculated per eq 6 using the boundary conditions $C(0) = 11 \text{ g m}^{-3}$, diffusion coefficient $D_{\text{O}_2}(5^\circ \text{C}) = 1.08 \times 10^{-4} \text{ m}^2 \text{ d}^{-1}$, $F_{\text{red}} = 0.36 \text{ g of O}_2 \text{ m}^{-2} \text{ d}^{-1}$, and DBL thickness $\delta = 0.82 \text{ mm}$, assuming that $C = 0$ at the sediment surface.

selected z_H values using the average $C(0)$, δ , and F_{red} values defined above. It is evident from Figure 2 that in lakes with $z_H > \sim 17 \text{ m}$, O_2 is not entirely depleted. The seasonally averaged mineralization, AHM, is therefore not limited by the O_2 concentration and can reach high values. On the contrary, in a lake with a hypolimnion as shallow as 7 m , however, O_2 is utilized completely after 83 d and AHM decreases at the constant rate F_{red}/z_H after O_2 is depleted (Figure 2). Thus, the earlier that O_2 is depleted (i.e., the smaller the z_H), the smaller the seasonally averaged AHM. For a highly eutrophic system, if it is completely homogenized during winter and starts with $C(0) = 11 \text{ mg L}^{-1}$ at the onset of a new season of stratification, a z_H value of 37 m is required for the average O_2 concentration to remain above the local management goal of 4 mg L^{-1} .

This model generates several important hypotheses which are discussed in detail below:

- In aerobic hypolimnia AHM equals the sum of (a) the zero-order sediment O_2 consumption rate, F_{red} , and (b) the diffusion of O_2 to the sediment surface, which increases linearly with increasing z_H up to $\sim 25 \text{ m}$.

Table 2. Fluxes of Reduced Substances from the Sediment ($\text{mmol m}^{-2} \text{d}^{-1}$) and the Estimated O_2 Equivalent Fluxes (F_{red}) Expressed ($\text{g of O}_2 \text{ m}^{-2} \text{d}^{-1}$)^a

lake	CH_4 flux	NH_4^+ flux	$\text{S}(-\text{II})$ flux	$\text{Mn}(\text{II})$ flux	$\text{Fe}(\text{II})$ flux	no. of measurements	F_{red}
Sempachersee	2.12	1.21				6 (May to Oct)	0.21
Hallwilersee	2.17	2.23		0.11		1	0.28
Murtensee	3.81	0.80		1.37	0.23	1	0.32
Pfäffikersee	4	1.40		0.61	1.00	1	0.36
Türlersee	4.9	1.80		0.51	0.67	1	0.44
Rotsee	4.05	1.85	1.31			6 (May to Oct)	0.46
Baldeggersee	4.52	4.07		0.24		2	0.55
average							0.37
std dev							0.12

^aTwo equivalents of O_2 were used for the oxidation of CH_4 , NH_4^+ , and $\text{S}(-\text{II})$, as well as 0.5 and 0.25 equiv of O_2 for the oxidation of $\text{Mn}(\text{II})$ and $\text{Fe}(\text{II})$, respectively, per eqs 1a–1e.

Table 3. Average Annual Fluxes of Net Epilimnion Export of Organic Carbon to the Hypolimnion and Gross Sedimentation Based on Sediment-Trap Data

lake	net export from epilimnion, $\text{g of C m}^{-2} \text{yr}^{-1}$	benthic gross sedimentation, $\text{g of C m}^{-2} \text{yr}^{-1}$	monitoring duration, month–year	sampling interval	ref
Baldeggersee	90 ± 5		3–94 to 10–96	1 day	M. Sturm, unpublished results
Greifensee	81	89	4–02 to 4–03	1 month	M. Sturm, unpublished results
Sempachersee	74 ± 22	77 ± 23	1–84 to 12–87	2 weeks	26
Sempachersee	50 ± 24	70 ± 34	1–88 to 1–93	2 weeks	R. Gächter, unpublished results
Zugersee north basin	100	97	3–82 to 3–83	3 weeks	27
Zugersee south basin	85	92	3–82 to 3–83	3 weeks	27

- (ii) AHM approaches an upper limit for $z_{\text{H}} > 25$ m, indicating an upper limit for carbon to be mineralized during the summer stagnation period.
- (iii) The sediment uptake rate of O_2 is controlled by the benthic O_2 concentration and δ , which is partly governed by wind exposition of a lake and resultant near-sediment boundary currents.
- (iv) Hypolimnetic O_2 consumption exceeds the values predicted in Figure 1 if the O_2 concentration is increased artificially in aerated/oxygenated lakes.
- (v) The relative importance of F_{red} and corresponding AHM decreases with increasing z_{H} and decreasing productivity, e.g., in meso- to oligotrophic lakes.

Intrinsic Sediment O_2 Consumption and Resultant F_{red} . F_{red} estimates are a function of the sediment composition and corresponding porewater concentrations resulting from early diagenetic processes in the sediment as well as the organic carbon content of the sediment. On the basis of porewater data from various studies (Table 2), measurements of reduced substances in the sediment porewater of six eutrophic lakes yielded an average F_{red} of $0.37 \pm 0.12 \text{ g of O}_2 \text{ m}^{-2} \text{d}^{-1}$, which compares excellently with F_{red} of $0.36 \text{ g of O}_2 \text{ m}^{-2} \text{d}^{-1}$ as estimated from AHM budgets of the seven shallowest lakes in Figure 1 and eq 3. Fluxes of CH_4 and NH_4^+ represent the largest fraction (on average >90%) of the reduced compounds. The results in Table 2 show differences in F_{red} of up to a factor of 2.5 between lakes. This may be caused by the differing intensities and durations of their eutrophication history. An additional factor may be that different methods of porewater extraction were used, e.g., during the Sempachersee and Rotsee studies.

F_{red} requires a greater percentage of the available O_2 when the hypolimnion is shallow because it is used up more quickly, and thus, the contribution of the O_2 flux into the sediment is decreased. The fraction of O_2 in a horizontal water layer that is consumed by reduced substances from the sediment gets larger as the sediment area per volume in contact with this water layer increases. Correspondingly, increased AHM is observed with lake depth. This phenomenon was observed for lakes of different depths or, rather, varying fractions of sediment area per volume, $z_{\text{H}}^{-1} = A_{\text{H}}/V_{\text{H}} \text{ (m}^{-1}\text{)}$. Figure SI-2 (Supporting Information) shows that the percentage of O_2 in the hypolimnion consumed by diffusion to the sediment increases proportionally with z_{H}^{-1} .

Maximum Flux of Particulate Organic Carbon to the Sediment. Figure 1 shows that AHM asymptotically approaches an upper limit when z_{H} of eutrophic lakes increases. Logically, this is to be expected as the productive surface zone of a lake expands only slightly (by a few meters) in the vertical direction regardless of the lake size;²² hence, primary production is limited to a maximum of $\sim 400\text{--}500 \text{ g of C m}^{-2} \text{yr}^{-1}$. For the eutrophic lakes evaluated in this study, measurements of net export from the epilimnion and benthic gross sedimentation rates are available from a number of sediment-trap studies (Table 3). Maximum net export rates of carbon from the trophic zone into the hypolimnion of these hypertrophic lakes are thus in a similar range with an upper estimate of $\sim 100 \text{ g of C m}^{-2} \text{yr}^{-1}$ despite very different P concentrations. Moreover, sediment-trap data in Table 3 also show that fluxes from bottom traps are not significantly different from those from traps directly below the epilimnion. Our results are supported by sediment-trap data from Bernasconi et al.,²³ which show primary production of $300 \text{ g of C m}^{-2} \text{yr}^{-1}$ and benthic sedimentation of $109 \text{ g of C m}^{-2} \text{yr}^{-1}$.

for Lake Lugano (a deep meromictic lake not included in our study). While z_H and corresponding mineralization in the water column do influence AHM via resultant sediment composition (e.g., labile organic matter) and F_{red} , on the basis of these sediment-trap data highlighting the influence of sediment O_2 uptake relative to overall O_2 consumption,^{24,25} we conclude that neglecting mineralization in the water column in the AHM model is justified.

On the basis of these sediment-trap data, we estimated AHM as a function of organic matter mineralization by calculating the difference between the benthic gross sedimentation (Table 3) and the net burial in the sediment. Long-term average net sedimentation rates of organic carbon for Baldeggersee, Greifensee, and Sempachersee were 27, 37, and 24 g of C $m^{-2} yr^{-1}$, respectively (B. Müller, unpublished results). Assuming that mineralization of newly deposited sediment in Table 3 mainly occurs within the ~ 200 d of stratification, we estimated AHM values of 1.09 ± 0.24 g of $O_2 m^{-2} d^{-1}$ for Baldeggersee, 0.90 g of $O_2 m^{-2} d^{-1}$ for Greifensee, and 0.92 ± 0.33 g of $O_2 m^{-2} d^{-1}$ for Sempachersee (1984–1987). These values match AHM estimates based on O_2 data perfectly for Baldeggersee (1.17 ± 0.17 g of $O_2 m^{-2} d^{-1}$; Figure 1) and Greifensee (0.71 ± 0.10 g of $O_2 m^{-2} d^{-1}$). The consistency with Sempachersee results is not as strong; however, the estimates are still within the range of significance ($AHM = 1.32 \pm 0.18$ g of $O_2 m^{-2} d^{-1}$). In view of the large errors involved with the quantification of both sediment-trap-based carbon fluxes and net sedimentation rates, the agreement of the AHM values estimated from carbon fluxes and AHM values estimated from O_2 consumption for both lakes supports the model capability.

Variation of the Diffusive Boundary Layer Thickness. The parameter δ is expected to vary with physical exposure to wind forcing and is therefore different for every lake and is also a function of time and depth. Figure 3 illustrates for Sempachersee

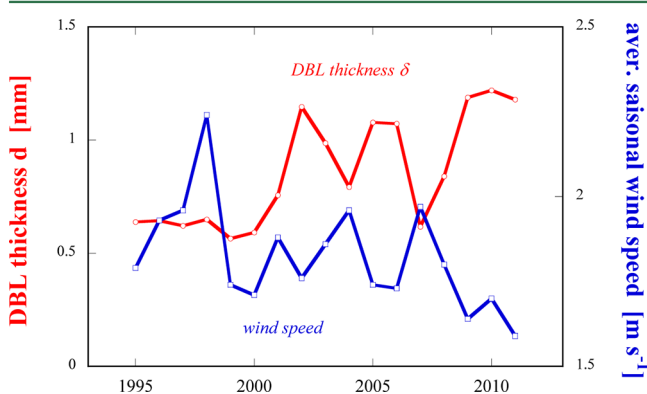


Figure 3. Diffusive boundary layer thickness δ estimated from AHM in Sempachersee using eq 6 relative to wind speed measured at the nearby weather station Egolzwil (<http://meteoneews.ch/en/Measurements/M06648000/Egolzwil>) averaged over the stratified season (April to October).

that wind speed and AHM were strongly inversely correlated, as expected, during 1995–2011. Lakes with higher bottom boundary currents facilitate thinner δ , while deeper and less turbulent zones result in thicker δ .²¹ The near-bottom O_2 concentration, which contributes to the driving force of O_2 flux into the sediment,²¹ is always less than the average concentration in the hypolimnion. Using the average hypolimnetic O_2 concentration in eq 5 therefore results in an overestimation of δ . Furthermore, in reality δ is typically thinner than the values

indicated by the fit in Figure 1 as shown by measurements obtained by Lorke et al.²⁰ Additionally, D_{O_2} , which was assumed constant for the model (eq 5), is a function of temperature and thus varies with the depth-dependent temperature of the hypolimnion.

Increased AHM in Aerated Lakes: Consequences of O_2 Availability. As δ is a function of wind, more energetic systems have a thinner δ and consequently higher O_2 uptake by the sediment. If aeration/oxygenation systems increase bottom boundary currents, this could subsequently enhance sediment O_2 uptake and cause higher AHM, as observed by Bryant et al.²⁸ Both aeration-induced increases in near-sediment O_2 concentration and decreases in δ result in enhanced mineralization of sedimentary organic matter and enhanced AHM^{29,30} as is demonstrated in Figure 1 (orange dots).

We hypothesize that the addition of O_2 by oxygenation or artificial mixing will not have the same effect in shallow and deep lakes. In shallow lakes where O_2 concentrations have been low in the past decades, we expect less organic carbon to be mineralized in the hypolimnion, resulting in a higher burial rate and a higher F_{red} . Conversely, deeper lakes likely have enhanced organic carbon mineralization and, subsequently, a lower F_{red} . Thus, increased O_2 content may be more difficult to achieve in shallower lakes relative to deeper ones in which a lower F_{red} would require less O_2 to be satisfied and hence facilitate most of the added O_2 remaining in the water body. Model results presented here are supported by Gantzer et al.,²⁹ who observed significantly higher O_2 depletion rates in the shallower of two oxygenated reservoirs.

The average AHM of all lakes investigated from our lake monitoring data set lies in a narrow range of 0.90 ± 0.30 g of $O_2 m^{-2} d^{-1}$ with a low interannual variability of only $\sim 12\%$ (Table 1). These results suggest that O_2 consumption is only weakly related to the trophic status of the lakes. This agrees with the observation that increased O_2 content during reoligotrophication of many lakes had little effect on AHM. In fact, as the mineralization of organic matter is a first-order kinetic process depending on the O_2 concentration, it may be observed that AHM still remains high after the lake trophic state improves. As a result of oligotrophication, deep mixing in winter could be more effective and lead to a higher spring O_2 level, which could then result even in an enhanced flux of O_2 into the sediment and hence lead to higher AHM.

AHM in Oligotrophic Lakes. As expected, the AHM of the nine deep meso- to oligotrophic lakes presented in Figure SI-3 (Supporting Information) did not fulfill the conditions of our model. Obviously, if the O_2 -storage capacity of a lake's hypolimnion exceeds a minimum limit, the correlation between AHM and z_H disappears. As a result, lakes that exceed a certain critical z_H are protected from becoming anoxic during summer stratification. However, if the lakes have sediments with a high content of organic matter from their recent eutrophic past, such as Lake Geneva, their O_2 consumption is still maximal and thus follows our model.

The net production of these oligotrophic lakes should be controlled by the amount of BAP available during the productive season. However, data for BAP loads were not collected during the lake monitoring campaigns evaluated in this study because these oligotrophic lakes were not at risk for becoming eutrophic. In oligotrophic lakes, F_{red} may be negligible and O_2 diffusion may govern AHM since the O_2 penetration depth often reaches up to several centimeters, as observed in Brienzensee³¹ and Lake

Baikal.³² Thus, all O₂ consumption likely occurs within the oxic sediment-surface zone with minimal contributions from F_{red} .

Comparison with AHOD of Eutrophic Lakes from the Literature. We evaluated the literature to obtain additional data with which to test our model. The general trend agrees with our data set. However, there is significant scatter, and AHOD values are often below our model estimates (Figure SI-4, Supporting Information). We argue that the main reason for this deviation is the neglect of the reduced compounds excluded from AHOD. Additional data deficits include incomplete information on trophic status and too short monitoring duration. Discussion and documentation are provided in the Supporting Information.

Limitations and Shortcomings of the Model. The model presented here uses a robust, simplified approach to characterize the complex and interconnected processes occurring in the hypolimnion. The model is based on the following simplifications.

We assumed a homogeneous hypolimnion and did not take into account that O₂ consumption rates increase with increasing dA/dV ratio, causing O₂ concentrations to decrease at deeper depths. In the model, this volume-proportional consumption is vertically integrated to an areal consumption. As we did not consider this process, the mathematical effect in fitting the data in Figure 1 is a slight underestimation of δ . Given that the DBL thickness is anyway a surrogate of a spatially and temporally varying function, we do not consider this as a significant deficit in the model.

As a further simplification, the parameter z_{H} was assumed to remain constant, while in reality it varies seasonally. Additionally, vertical diffusive transport of O₂ between the hypolimnion and the overlying metalimnion, which can be a sink or a source for O₂ during the stratified season, was neglected.⁷

We simplified and separated the O₂-consuming processes at the sediment–water interface. O₂ profiles were idealized to decrease to zero at the sediment surface (second part of eq 3), while in reality O₂ often penetrates the sediment up to several millimeters in mesotrophic lake sediments (e.g., refs 20, 33, and 34). Furthermore, reduced substances diffusing from the sediment are assumed to pass through the location of maximum O₂ consumption and diffuse from the sediment into the hypolimnion before oxidation occurs.

F_{red} as determined from Figure 1 data is an averaged value. However, the true behavior of F_{red} may show some spatial and/or seasonal variations. First, F_{red} is not constant over the entire A_{H} but instead may be greatest at the deepest sites and decrease toward shallower depths due to sediment focusing.³⁵ In regions strongly affected by aeration/oxygenation, F_{red} may be increased due to increased precipitation of oxide particles.²⁸ Second, F_{red} may vary seasonally as this parameter depends on reduced-species concentration gradients between sediment porewater and the overlying water, which are influenced by seasonally variable bottom-boundary mixing. Similar to diffusive O₂ flux into the sediment, F_{red} can also be influenced by δ . Ebullition of CH₄ is assumed not to affect the O₂ balance substantially, as the release of bubbles is concentrated on shallow delta regions, fueled mainly from allochthonous OM fluxes into the lake from the drainage area.³⁶

This model includes only two—but the most essential—hypolimnetic O₂ depletion processes. Despite the various deficits related to this simplification and despite using averaged values for the three most relevant model parameters, the agreements between model results and several thousands of measured hypolimnetic O₂ contents in eleven eutrophic lakes is striking. This model allows estimation of AHM rates of eutrophic lakes,

including the effect of artificial aeration/oxygenation. Lake-specific parameters such as δ , which depends on turbulence, and F_{red} , which is governed by lake trophic status, were adapted over all lakes presented in Figure 1. When the model is applied to a specific lake, its predictive power is even more enhanced when lake-specific parameters are applied.

■ ASSOCIATED CONTENT

● Supporting Information

Figure SI-1 showing four examples of the seasonal development of temperature and O₂ depth profiles selected to demonstrate the determination of the mean epilimnion thickness, Figure SI-2 showing the relationship between z_{H} and AHM of 10 mesotrophic and oligotrophic lakes, with corresponding hydrological data provided in Table SI-1, detailed formulations and solutions of integrals of model equations, Table SI-2 giving AHM estimates where NO₃[−] is included as an oxidant in addition to O₂, Figure SI-3 showing that the fraction of O₂ consumed by reduced substances diffusing from the sediment increases with decreasing z_{H} , discussion and comparison of our AHM model predictions and literature data for AHOD, and Figure SI-4 correlating model predictions with AHOD data obtained from the literature plotted as a function of the estimated z_{H} , with Table SI-3 providing corresponding data and references. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The Commission Internationale pour la Protection des Eaux du Léman (CIPEL) and Data SILA, Database SOERE-INRA, of Thonon-les-Bains, France, are acknowledged for providing monitoring data for Lake Geneva and Lac d'Annecy. Lake-monitoring data sets were also obtained from the following: Türlensee, Greifensee, Pfäffikersee, Walensee, and Lake Zürich from Amt für Abfall, Wasser, Energie und Luft, AWEL, Zürich; Murtensee from Service de l'environnement, Fribourg; Hallwilersee from Amt für Umweltschutz, Aargau; Thunersee and Brienersee from the Amt für Umweltschutz, Bern; Aegerisee, Neuenburgersee, and Lake Constance from the central database of the Swiss Federal Office for the Environment, FOEN. The valuable comments of four anonymous reviewers as well as those of René Gächter and Martin Schmid on an earlier version of this manuscript are acknowledged. This publication is based upon work supported by Eawag and the United States National Science Foundation (NSF) under Grant EAR-PF 0848123.

■ REFERENCES

- (1) Vollenweider, R. A. *The Scientific Basis of Lake Eutrophication, with Particular Reference to Phosphorus and Nitrogen as Eutrophication Factors*; Technical Report DAS/DSI/68.27; Organisation for Economic Co-operation and Development (OECD): Paris, 1968; p 159.
- (2) Schindler, D. W. Recent advances in the understanding and management of eutrophication. *Limnol. Oceanogr.* **2006**, *51*, 356–363.
- (3) Hering, J. G.; Hoehn, E.; Klink, A.; Maurer, M.; Peter, A.; Reichert, P.; Robinson, C. T.; Schirmer, K.; Schirmer, M.; Stamm, C.; Wehrli, B. Moving targets, long-lived infrastructure, and increasing needs for integration and adaptation in water management: an illustration from Switzerland. *Environ. Sci. Technol.* **2012**, *46* (1), 112–118.

- (4) Gächter, R.; Wehrli, B. Ten years of artificial mixing and oxygenation: no effect on the internal phosphorus loading of two eutrophic lakes. *Environ. Sci. Technol.* **1998**, *32*, 3659–3665.
- (5) Wehrli, B.; Lotter, A. F.; Schaller, T.; Sturm, M. High-resolution varve studies in Baldeggersee (Switzerland): project overview and limnological background data. *Aquat. Sci.* **1997**, *59*, 285–294.
- (6) Hutchinson, G. E. On the relation between the oxygen deficit and the productivity and typology of lakes. *Int. Rev. Gesamten Hydrobiol. Hydrogr.* **1935**, *36*, 336–355.
- (7) Matzinger, A.; Müller, B.; Niederhauser, P.; Schmid, M.; Wüest, A. Hypolimnetic oxygen consumption by sediment-based reduced substances in former eutrophic lakes. *Limnol. Oceanogr.* **2010**, *55*, 2073–2084.
- (8) Chapra, S. C. C.; Canale, R. P. Long-term phenomenological model of phosphorus and oxygen for stratified lakes. *Water Res.* **1991**, *25*, 707–715.
- (9) Matthews, D. A.; Effler, S. W. Long-term changes in the areal hypolimnetic oxygen deficit (AHOD) of Onondaga Lake: evidence of sediment feedback. *Limnol. Oceanogr.* **2006**, *51*, 702–714.
- (10) Rippey, B.; McSorley, C. Oxygen depletion in lake hypolimnia. *Limnol. Oceanogr.* **2009**, *54*, 905–916.
- (11) Cornett, R. J.; Rigler, F. H. Hypolimnetic oxygen deficits: their prediction and interpretation. *Science* **1979**, *205*, 580–581.
- (12) Cornett, R. J.; Rigler, F. H. The areal hypolimnetic oxygen deficit: an empirical test of the model. *Limnol. Oceanogr.* **1980**, *25* (4), 672–679.
- (13) Beutel, M. Hypolimnetic anoxia and sediment oxygen demand in California drinking water reservoirs. *Lake Reservoir Manage.* **2003**, *19*, 208–221.
- (14) McGinnis, D. F.; Lorke, A.; Wüest, A.; Stöckli, A.; Little, J. C. Interaction between a bubble plume and the near field in a stratified lake. *Water Resour. Res.* **2004**, *40*, W10206.
- (15) Singleton, V. L.; Little, J. C. Designing hypolimnetic aeration and oxygenation systems: a review. *Environ. Sci. Technol.* **2006**, *40* (24), 7512e7520.
- (16) Burns, N. M. Using hypolimnetic dissolved oxygen depletion rates for monitoring lakes. *N. Z. J. Mar. Freshwater Res.* **1995**, *29*, 1–11.
- (17) Carpenter, J. H. The accuracy of the Winkler method for dissolved oxygen analysis. *Limnol. Oceanogr.* **1965**, *10*, 135–140.
- (18) German Standard Methods for the Examination of Water, Wastewater, and Sludge (in German); Wiley-VCH: Weinheim, Germany, 2002.
- (19) Müller, B.; Wang, Y.; Dittrich, M.; Wehrli, B. Influence of organic carbon decomposition on calcite dissolution in surficial sediments of a freshwater lake. *Water Res.* **2003**, *37*, 4524–4532.
- (20) Lorke, A.; Müller, B.; Maerki, M.; Wüest, A. Breathing sediments: the control of diffusive transport across the sediment-water interface by periodic boundary-layer turbulence. *Limnol. Oceanogr.* **2003**, *48* (6), 2077–2085.
- (21) Bryant, L. D.; Lorrai, C.; McGinnis, D. F.; Brand, A.; Wüest, A.; Little, J. C. Variable sediment oxygen uptake in response to dynamic forcing. *Limnol. Oceanogr.* **2010**, *55* (2), 950–964.
- (22) Wetzel, R. *Limnology*; Academic Press: New York, 2001.
- (23) Bernasconi, S.; Barbieri, A.; Simona, M. Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano. *Limnol. Oceanogr.* **1997**, *42* (8), 1755–1765.
- (24) Glud, R. Oxygen dynamics in marine sediments. *Mar. Biol. Res.* **2008**, *4* (4), 243–289.
- (25) Higashino, M.; Gantzer, C. J.; Stefan, H. G. Diffusive boundary layer development above a sediment-water interface. *Water Environ. Res.* **2004**, *76* (4), 292–300.
- (26) Gächter, R.; Meyer, J. S. Mechanisms controlling fluxes of nutrients across the sediment-water interface in a eutrophic lake. In *Sediments: Chemistry and Toxicity of In-Place Pollutants*; Baudo, R., Giesy, J., Muntau, H., Eds.; Lewis: Ann Arbor, MI, 1990; Chapter 5, pp 131–162.
- (27) Bloesch, J.; Sturm, M. Settling flux and sinking velocities of particulate phosphorus (PP) and particulate organic carbon (POC) in Lake Zug, Switzerland. In *Sediments and Water Interactions*; Sly, P. G., Ed.; Springer: New York, 1986; pp 481–490.
- (28) Bryant, L. D.; Hsu-Kim, H.; Gantzer, P. A.; Little, J. C. Using the source water as the solution: controlling Mn release at the sediment-water interface via hypolimnetic oxygenation. *Water Res.* **2011b**, *45*, 6381–6392.
- (29) Gantzer, P. A.; Bryant, L. D.; Little, J. C. Effect of hypolimnetic oxygenation on oxygen depletion rates in two water-supply reservoirs. *Water Res.* **2009**, *43*, 1700–1710.
- (30) Bryant, L. D.; Gantzer, P. A.; Little, J. C. Increased sediment oxygen uptake caused by oxygenation-induced hypolimnetic mixing. *Water Res.* **2011a**, *45*, 3692–3703.
- (31) Müller, B.; Finger, D.; Sturm, M.; Prasuhn, V.; Haltmeier, T.; Bossard, P.; Hoyle, C.; Wüest, A. Present and past bio-available phosphorus budget in the ultra-oligotrophic Lake Brienz. *Aquat. Sci.* **2007**, *69*, 227–239.
- (32) Maerki, M.; Müller, B.; Wehrli, B. Microscale mineralization pathways in surface sediments: a chemical sensor study in Lake Baikal. *Limnol. Oceanogr.* **2006**, *51* (3), 1342–1354.
- (33) Maerki, M.; Müller, B.; Dinkel, C.; Wehrli, B. Mineralization pathways in lake sediments with different oxygen and organic carbon supply. *Limnol. Oceanogr.* **2009**, *54* (2), 428–438.
- (34) Müller, B.; Maerki, M.; Dinkel, C.; Stierli, R.; Wehrli, B. In-situ measurements of lake sediments using ion-selective electrodes with a profiling lander system. In *Environmental Electrochemistry: Analyses of Trace Element Biogeochemistry*; Taillefer, M.; Rozan, T. F., Eds.; American Chemical Society Symposium Series 811; American Chemical Society: Washington, DC, 2002; pp 126–143.
- (35) Schaller, T.; Wehrli, B. Geochemical focusing of manganese in lake sediments—an indicator of deep-water oxygen conditions. *Aquat. Geochem.* **1997**, *2* (4), 359–378.
- (36) Schubert, C. J.; Diem, T.; Eugster, W. Methane emissions from a small wind shielded lake determined by eddy covariance, flux chambers, anchored funnels, and boundary model calculations: a comparison. *Environ. Sci. Technol.* **2012**, *46* (8), 4515–4522.
- (37) Schubert, C.; Lucas, F. S.; Durisch-Kaiser, E.; Stierli, R.; Diem, D.; Scheidegger, O.; Vazquez, F.; Müller, B. Oxidation and emission of methane in a monomictic lake (Rotsee, Switzerland). *Aquat. Sci.* **2010**, *72*, 455–466.
- (38) Sigg, L.; Johnson, A. C.; Kuhn, A. Redox conditions and alkalinity generation in a seasonally anoxic lake (Lake Greifen). *Mar. Chem.* **1991**, *36*, 9–26.
- (39) Moosmann, L.; Gächter, R.; Müller, B.; Wüest, A. Is phosphorus retention in autochthonous lake sediments controlled by oxygen or phosphorus? *Limnol. Oceanogr.* **2006**, *51*, 763–771.
- (40) Masson, S.; Angeli, N.; Guillard, J.; Pinel-Alloul, B. Diel vertical and horizontal distribution of crustacean zooplankton and young of the year fish in a sub-alpine lake: an approach based on high frequency sampling. *J. Plankton Res.* **2001**, *23* (10), 1041–1060.
- (41) Anneville, O.; Ginot, V.; Angeli, N. Restoration of Lake Geneva: expected versus observed responses of phytoplankton to decreases in phosphorus. *Lakes Reservoirs: Res. Manage.* **2002**, *7*, 67–80.