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Hypolimnetic oxygen depletion rates in deep lakes: Effects of trophic state and organic matter accumulation

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Abstract

This study investigated the consumption of oxygen (O_2) in 11 European lakes ranging from 48 m to 372 m deep. In lakes less than ~ 100 m deep, the main pathways for O_2 consumption were organic matter (OM) mineralization at the sediment surface and oxidation of reduced compounds diffusing up from the sediment. In deeper lakes, mineralization of OM transported through the water column to the sediment represented a greater proportion of O_2 consumption. This process predominated in the most productive lakes but declined with decreasing total phosphorous (TP) concentrations and hence primary production, when TP concentrations fell below a threshold value of ~ 10 mg P m^{-3}. Oxygen uptake by the sediment and the flux of reduced compounds from the sediment in these deep lakes were 7.9–10.6 and 0.6–3.6 mmol m^{-2} d^{-1}, respectively. These parameters did not depend on the lake's trophic state but did depend on sedimentation rates for the primarily allochthonous or already degraded OM. These results indicate that in lakes deeper than ~ 100 m, mineralization of autochthonous OM is mostly complete by the time of sedimentary burial. This explains why hypolimnetic O_2 concentrations improve more rapidly following TP load reduction in deeper lakes relative to shallower lakes, where larger sediment-based O_2 consumption by settled OM and release of reduced substances may inhibit the restoration of hypolimnetic O_2 concentrations.

Sufficient O_2 concentrations in the hypolimnia of lakes are essential for maintaining habitats, supporting fish reproductive cycles, and ensuring reliable drinking water sources. Oxygen concentrations are thus a key parameter for lake management. In the middle of the 20th century, increasing phosphorous (P) concentrations contributed to drastic increases in primary production and subsequent transport of OM to deep hypolimnetic waters. Aerobic mineralization of OM and the release of anaerobically produced compounds such as methane (CH_4) and ammonium (NH_4^+) into bottom waters are common contributors to hypolimnetic O_2 depletion. Lacustrine OM mineralization generally occurs in three different domains. These include (1) the water column during settling of organic particles (Livingstone and Imboden 1996), (2) sediment surfaces subject to intensive remineralization and biological reworking (Burns 1995), and (3) underlying, deeper sediments that host gradual but continuous production of reduced substances (Carignan and Lean 1991; Steinsberger

et al. 2017). O_2 consumption rates for each of these locations have been respectively termed (1) water column mineralization rate in the hypolimnion (WCM), (2) sediment oxygen uptake (SOU), and (3) flux of reduced compounds from the sediment, F_{red}, as converted to O_2 consumption equivalents (Matzinger et al. 2010; Müller et al. 2012). The areal hypolimnetic mineralization (AHM) represents the sum of all three O_2 consumption processes over the whole hypolimnion.

For fully productive (eutrophic) lakes of less than ~ 100 m depth, SOU (OM mineralization on the sediment surface) and F_{red} (reduced compounds diffusing from interstitial fluids in deeper sediments) represent the primary sites of O_2 consumption (Matthews and Effler 2006; Müller et al. 2012). In deeper (> 100 m) lakes such as the Great Laurentian Lakes, WCM and SOU govern O_2 depletion (Charlton 1980). Studies of Lakes Michigan (Thomsen et al. 2004), Erie (Edwards et al. 2005; Smith and Matisoff 2008), and Superior (Li et al. 2012) have further demonstrated the importance of SOU and/or WCM as O_2 sinks in these lakes. A study of the highly productive and deep Lake Geneva by Schwefel et al. (2018) showed that, as with the Great Lakes, O_2 consumption primarily occurred in the water column rather than near or in the sediment.

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In general, deep lakes such as Baikal or Superior store enough O$_2$ in their large hypolimnia to prevent anoxia in bottom waters, assure aerobic OM remineralization and limit the production of reduced substances (Müller et al. 2005; Li et al. 2012). Even in the very productive and deep Lake Geneva, which exhibits a TP concentration of ~ 24 mg P m^{-3} (average from 2008 to 2018) and a carbon assimilation rate of ~ 250 g C m^{-2} yr^{-1} (Anneville and Pelletier 2000; Soomets et al. 2019), sediment characteristics resemble those of an oligotrophic lake with low TOC content (~ 1%), very small fluxes of CH$_4$ and NH$_4^+$ from the sediment and limited O$_2$ consumption at the sediment–water interface (Steinsberger et al. 2017; Schwefel et al. 2018). The high fraction of WCM (~ 70%) on the total AHM diminishes the oxidizing capacity of the settling material on its way to the sediment. Given the mostly, already degraded OM, SOU only contributed about 27% to AHM. The O$_2$ made available by a large hypolimnion for extensive oxic mineralization of settling OM results in only a marginal amount of OM burial in sediments.

In shallower lakes (< 100 m depth) with similar productivity, shorter settling distances may limit (oxic) mineralization in the water column. This could lead to accumulation and burial of large volumes of mostly un-mineralized OM in sediments. The subsequent slow but persistent release of reduced compounds generated by anaerobic OM degradation further consumes O$_2$ and often impedes later restoration measures (Wehrli et al. 1997).

In shallow lakes, this "sediment memory effect" or "sediment legacy" and associated release of reduced substances from the sediment may account for up to 80% of the O$_2$ depletion in the hypolimnion even with measures aimed at reestablishing oligotrophic conditions (Matthews and Effler 2006; Carey et al. 2018). Although this effect has been documented in lakes of up to ~ 100 m depth, its potential impact on deeper lakes is not as well understood (Matzinger et al. 2010). In most deep lakes, the contribution of different O$_2$ sinks to overall hypolimnion O$_2$ depletion remains debated or unknown.

This study aimed to determine the location and intensity of O$_2$ consumption in eight lakes of > 100 m depth and three lakes of < 100 m depth. We determined O$_2$ consumption rates at the sediment surface, fluxes of reduced compounds and O$_2$ depletion rates in the water column using lake monitoring data, O$_2$ microprofile measurements and simultaneous sediment pore-water analysis. Oxygen consumption was characterized and interpreted in terms of spatial location, trophic state, hypolimnion depth, and accumulation of OM.

Material and methods

Site description

Sediment cores of the lakes characterized in Table 1 were retrieved at the deepest locations of each lake except for Lakes Maggiore, Lucerne, and Constance. For Lake Maggiore, sediment cores were collected from 273 m depth at the deepest site of the Swiss part of the lake. For Lake Lucerne, sediment was collected in the deepest part of the Vitznau basin at 150 m water depth. For Lake Constance, sediment was collected at 150 m depth in the main basin. All sediment cores were collected during the lake's stratified period (between May and October). Table S1 summarizes sampling details, location, and dates. The two shallowest lakes, Hallwil and Baldegg, both experience recurring hypolimnetic hypoxia caused by high primary production. Both lakes are artificially aerated during summer stratification and mixing has been supported by bubble plumes during overturn since the 1980s. Hypolimnetic O$_2$ sinks are thus influenced by artificially elevated O$_2$ concentrations introduced by lake restoration efforts.

Sampling procedure

For each sampling site, four sediment cores were collected with a gravity corer. These cores were subjected to individual

Table 1. Physiographic and limnological characteristics of the lakes investigated by this study. A_H and V_H represent the hypolimnion area and volume, respectively. z_H is the mean hypolimnion depth (V_H/A_H). The hypolimnion was defined as the water body below 15 m water depth.

Lake	Max. depth (m)	Volume (km^3)	Surface (km^2)	A_H (km^2)	V_H (km^3)	z_H (m)
Maggiore (MAG)	372	37.6	213	196	34.5	176
Geneva (GEN)	310	89.1	582	534	80.8	151
Brienz (BRI)	260	5.0	29.8	27.8	4.59	165
Constance (CON)	253	47.8	482	403	41.4	103
Thun (THU)	217	6.46	47.9	43.9	5.78	132
Lucerne (LUC)	214	2.30	22	21.1	1.98	93.9
Neuchâtel (NEU)	154	13.8	218	156	11.1	71.3
Walensee (WAL)	151	2.51	24.1	22.8	2.15	94.3
Aegeri (AEG)	81	0.35	7.21	6.4	0.26	46.6
Baldegg (BAL)	66	0.17	5.22	4.53	0.13	27.6
Hallwil (HAL)	48	0.29	9.95	8.58	0.19	22.6

measurements of sediment pore water, CH_4, O_2 micro-optode profiles, and bulk analysis of sediment chemical and physical properties.

Sediment cores subjected to bulk analysis were stored in a cold room (4°C) until processing. The cores were sampled as 0.5 to 1 cm sections, weighed and freeze-dried. Water content was calculated from the weight difference before and after drying. Sediment porosity was estimated from water content, sediment density, and TOC content (Och et al. 2012). After grinding with an agate mortar, the sediment was further analyzed for TOC/TN with a Euro EA 3000 (HEKAtech). Total organic carbon mass accumulation rates (TOC-MAR) were determined for each site at depths between 1 and 10 cm sediment depths in 5 mm spatial resolution. Estimation of TOC-MAR followed detailed methods outlined in Steinsberger et al. (2017). Sedimentation rates were derived from literature sources or estimated from ^{210}Pb and ^{137}Cs measurements as reported from prior analyses of the respective lake sediments.

For CH_4 and sediment pore-water analysis, 60-cm-long PVC liners with predrilled and taped holes (diameter 1.2 cm and 2 mm, respectively) were used. Syringes with clipped tips were used to sample 2 cm^3 of sediment aliquots for CH_4 analysis. Aliquots were directly transferred to 113.7 mL flasks containing 2 mL of 7 M NaOH, then capped, stored, and prepared for GC headspace analysis. The sampling resolution was 1 cm for the upper 10 cm, 2 cm for the middle 10 cm and 3 cm from 20 to 35 cm sediment depth.

Sediment pore water was extracted using MicroRhizon filter tubes of 1.5 mm diameter (Torres et al. 2013). Punching through the taped pre-drilled holes allowed for withdrawal of 10–50 μL of sediment pore water. This pore water was transferred to a flip tube and immediately injected onto a capillary electrophoresis (CE)-C^4D column (Section 1.3). Relative to the sediment–water interface, pore water was sampled every 5 mm for the upper 5 cm, every 1 cm for the following 5 cm and every 2 cm from 10 to 20 cm sediment depth.

The fourth core was used to sample bottom water for O_2 concentration using the Winkler method. Vertical concentration profiles of O_2 in the sediment cores were performed with a PreSens O_2 micro-optode mounted onto an automated micromanipulator (Section 1.3).

Oxygen and sediment pore-water analysis

Sediment pore-water analysis and O_2 concentration profiles were measured directly on site at each lake. Sediment pore-water samples were analyzed for anions and cations with two portable CE devices, each with a capacitively coupled contactless conductivity detector (C^4D) calibrated directly on site (Kubáň et al. 2007). These devices were set at 15 kV and 0.5 μA to achieve complete separation of cations (NH_4^+, K^+, Ca^{2+}, Na^+, Mg^{2+}, Fe^{2+}, Mn^{2+}) and anions (Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, $H_2PO_4^-$) within 8 min (Torres et al. 2013). All calibration standards and the background electrolyte buffer were prepared from corresponding salts with ultrapure water (Merck)

immediately prior to each sampling campaign. These were checked using a multi-cation standard (Fluka) and a multi-anion standard (Roth). Standard deviations of all calibration measurements were < 5%.

The diffusive fluxes of reduced substances (J_{CH_4}, J_{NH_4}, $J_{Mn(II)}$, $J_{Fe(II)}$) from the sediments were calculated from pore-water concentration gradients (Supporting Information Fig. S1). The one-dimensional steady-state diffusion model by Epping and Helder (1997) was adapted to calculate fluxes:

$$J_i = -\frac{D}{G} * \frac{dC_i}{dx} \tag{1}$$

For J in mmol m^{-2} d^{-1}, D represents the diffusion coefficient based on temperature corrected values from Li and Gregory (1974), G represents porosity corrected formation factor ($1.02 * porosity^{-1.81}$) for clay-silt sediment, and $\frac{dC_i}{dx}$ represents the concentration gradient of species i (Maerki et al. 2004). Based on the redox stoichiometry (Eq. 2), the estimated fluxes were converted to O_2 equivalents (mmol O_2 m^{-2} d^{-1}) (Matzinger et al. 2010; Müller et al. 2012) as follows:

$$F_{red} = 2 * J_{CH_4} + 2 * J_{NH_4} + 0.5 * J_{Mn(II)} + 0.25 J_{Fe(II)} \tag{2}$$

O_2 measurements were conducted with a PreSens O_2 micro-optode with a flat tip size of 230 μm, a detection limit of 0.64 μmol O_2 L^{-1} and a response time < 10 s. The micro-optode was mounted to an automated micromanipulator. O_2 profiles were taken between 2 cm above and 3 cm below the sediment–water interface at 100 μm intervals and a penetration speed of 100 μm s^{-1} stopping for each measurement, completing a full profile in < 9 min. The O_2 penetration depth was defined as the sediment depth where O_2 concentrations dropped below 3 μmol O_2 L^{-1}. The O_2 micro-optode was calibrated in the laboratory with a two-point calibration. During the on-site measurements, standard deviation for O_2 measurements was typically ~ 11%. Up to nine replicate measurements were taken at different positions for each core.

Simultaneous O_2 measurements were not performed in Lakes Hallwil, Geneva, or Constance. Data from Bierlein et al. (2017) (Lake Hallwil), Schwefel et al. (2018) (Lake Geneva), and Sobek et al. (2009) (Lake Constance) were used for comparison instead.

The SOU flux was calculated similar to the flux of reduced substances (Eq. 1). Fluxes of the other two main electron acceptors, sulfate (SO_4^{2-}) and nitrate (NO_3^-), were converted to O_2 equivalents and added to SOU (Müller et al. 2007):

$$SOU = J_{O_2} + 1.25 * J_{NO_3} + 2 * J_{SO_4} \tag{3}$$

Areal hypolimnetic and water column mineralization

Based on monthly monitoring data, average AHMs for the past 10 years (2007–2017) were calculated from differences in

hypolimnetic O_2 content (> 15 m water depth) as measured between maximum values after winter mixing (February to April) and minimum values from October to November.

If reduced substances such as NH_4^+ and/or CH_4 occurred in bottom waters, they were included in the budget with their O_2 equivalents (Matzinger et al. 2010). WCM was calculated by subtracting SOU and F_{red} from AHM as:

$$AHM = SOU + F_{red} + WCM \tag{4}$$

$$WCM = AHM - \left(2 * J_{CH_4} + 2 * J_{NH_4} + 0.5 * J_{Mn(II)} + 0.25 * J_{Fe(II)}\right) - \left(J_{O_2} + 1.25 * J_{NO_3} + 2 * J_{SO_4}\right) \tag{5}$$

Comparability and limitations of SOU, F_{red}, and WCM parameters

Hypolimnetic O_2 sinks fundamentally depend on aerobic or anaerobic OM mineralization. Although the scale and biogeochemical processes may differ, these sinks are comparable because all fluxes are normalized to the hypolimnion area and expressed as O_2 equivalents (mmol O_2 m^{-2} d^{-1}). However, spatial and temporal variation may influence the individual size of the O_2 sinks.

Sediment-based O_2 sinks, F_{red}, and SOU are controlled by the amount of settled OM and are therefore sensitive to spatial effects such as sediment focusing. Gravitational slumping or wind forcing can resuspend fine-grained, organic-rich material, and transport it from littoral areas to deeper parts of lakes (Lehman 1975; Bloesch and Uehlinger 1986; Carignan and Lean 1991). Seasonal variations may also influence SOU since hypolimnetic O_2 concentrations tended to decrease until the end of the stratified season. A single O_2 measurement may therefore over- or underestimate annual average SOU values. Seasonal variation in F_{red} is less relevant since it depends only indirectly on fluctuating OM input or overlying O_2

concentrations (Frenzel et al. 1990; Schwefel et al. 2018; Steinsberger et al. 2019). By contrast, seasonal variation in primary production and associated settling and mineralization throughout the hypolimnetic water column strongly influence WCM but this variation is imbedded in yearly average AHM calculations.

Results

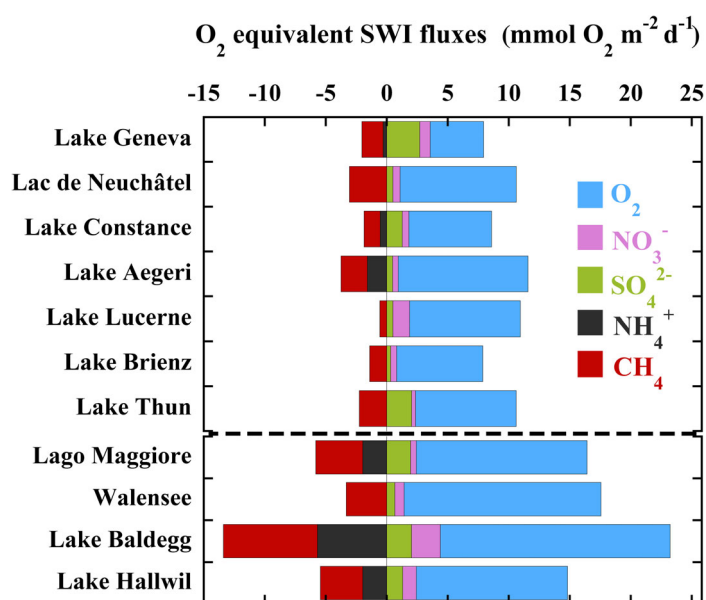### Fluxes of reduced substances from the sediment

Typical sediment concentration profiles of CH_4, NH_4^+, Fe(II), Mn(II), O_2, NO_3^-, and SO_4^{2-} are shown in the Supporting Fig. S1. Table 2 summarizes fluxes (J) of all measured species converted to O_2 equivalents from the 11 lakes.

In lakes deeper than 100 m, F_{red} showed similar low values of between 0.6 and 3.6 mmol O_2 m^{-2} d^{-1}. Shallower Lakes Hallwil, Baldegg, and Aegeri exhibited higher F_{red} values of between 4.0 mmol O_2 m^{-2} d^{-1} (Lake Aegeri) and 13.8 mmol O_2 m^{-2} d^{-1} (Lake Baldegg).

CH_4 and NH_4^+ represented the largest contributions to F_{red}. $J_{Fe(II)}$ and $J_{Mn(II)}$ were comparatively negligible and contributed on average only 1% and 2%, respectively, even though deeper parts of the sediment (> 10 cm depth) exhibited high sediment pore-water concentrations. Lago Maggiore sediment pore water, for example, contained 0.7 mmol Mn(II) L^{-1} and Lake Walensee sediment pore water contained 0.8 mmol Fe(II) L^{-1}. In lakes of > 100 m depth, NH_4^+ and CH_4 pore-water concentrations were at or below detection limits in the uppermost sediment layers (sometimes down to 5 cm). These values increased to 0.3–0.6 mmol L^{-1} (NH_4^+) and 2–7 mmol L^{-1} (CH_4) downcore (*see* Supporting Information Fig. S1). Except for Lago Maggiore, NH_4^+ did not reach the sediment surface but was oxidized within the uppermost centimeter. Here, J_{CH_4} represented up to 99% of F_{red} (Fig. 1). In the shallower Lakes Hallwil, Baldegg, and Aegeri (< 100 m depth),

Table 2. Sediment pore-water fluxes of reduced and oxidized species expressed as O_2 equivalents in mmol O_2 m^{-2} d^{-1}. Reduced species are summed as F_{red} and oxidants as SOU. Values of Lake Constance are averages from three sediment cores. Lakes are sorted according to decreasing mean hypolimnion depth.

Lake	J_{CH_4}	$J_{NH_4^+}$	$J_{Fe(II)}$	$J_{Mn(II)}$	F_{red}	J_{O_2}	$J_{NO_3^-}$	$J_{SO_4^{2-}}$	*SOU*
Maggiore	3.85	1.96	0.04	0.13	5.97	14.0	0.47	1.95	16.4
Geneva	1.74	0.30	0.01	0.03	2.07	4.48	0.86	2.7	8.04
Brienz	1.40	0	0	0.02	1.42	7.06	0.48	0.33	7.87
Constance	1.31	0.54	0.04	0.11	2.02	6.78	0.53	1.28	8.59
Thun	2.25	0	0	0.05	2.30	8.24	0.32	2.05	10.6
Lucerne	0.57	0	0.03	0.03	0.62	9.08	1.37	0.50	11.0
Neuchâtel	3.06	0	0.01	0.01	3.08	9.52	0.60	0.50	10.6
Walensee	3.32	0	0.07	0.18	3.57	16.2	0.76	0.66	17.6
Aegeri	2.15	1.59	0.11	0.11	3.96	10.6	0.46	0.48	11.6
Baldegg	7.71	5.68	0.25	0.11	13.8	18.8	2.36	2.04	23.2
Hallwil	3.48	1.96	0.13	0.03	5.60	12.4	1.10	1.32	14.8

O_2 equivalent SWI fluxes (mmol O_2 m^{-2} d^{-1})

Fig. 1. Flux at the sediment-water-interface (SWI) expressed in O_2 equivalents (mmol O_2 m^{-2} d^{-1}) of the main reduced substances, NH_4^+ and CH_4 (shown negatively scaled as black and red bars), and oxidants, O_2, SO_4^{2-}, and NO_3^- (positively scaled as light blue, green, and purple bars, respectively). Lakes were sorted according to F_{red}. Fluxes of Mn(II) and Fe(II) were negligible and are not shown.

in addition to J_{CH_4} (54% to 62%), J_{NH_4} was responsible for the remaining fraction of F_{red} (Fig. 1; ~ 40%).

Sediment oxygen uptake and penetration depths

Among lakes deeper than 100 m, SOU rates ranged only from 7.9 to 11.0 mmol O_2 m^{-2} d^{-1}. However, SOU values in Lakes Maggiore (16.4 mmol O_2 m^{-2} d^{-1}) and Walensee (17.6 mmol O_2 m^{-2} d^{-1}) were exceptionally high and resembled the SOU average of 19.0 mmol O_2 m^{-2} d^{-1} measured from the shallower and more productive Lakes Hallwil and Baldegg.

All lakes showed high O_2 concentrations in the hypolimnion (> 0.19 mmol O_2 L^{-1}, Supporting Information Fig. S2). However, penetration depths into the sediment were low (between 2.0 ± 1.0 mm in Lake Baldegg and 6.3 ± 0.8 mm in Lake Brienz, *see* Table 4) and did not correlate with bottom water O_2 concentrations. J_{O_2} ranged from 4.4 mmol O_2 m^{-2} d^{-1} in Lake Geneva to 18.8 mmol O_2 m^{-2} d^{-1} in Lake Baldegg (Table 2). J_{O_2} contributed an average of 78 ± 13% to total SOU. J_{NO_3} and J_{SO_4} varied between 0.3–2.4 and 0.3–2.0 mmol O_2 m^{-2} d^{-1} and respectively represented 6.7% ± 3.2% and 11.2% ± 9.1% of SOU. For lakes with high hypolimnetic NO_3^- and/or SO_4^{2-} concentrations (> 0.4 mmol L^{-1}; Lakes Geneva and Thun), combined J_{NO_3} and J_{SO_4} represented up to 45% of SOU (Fig. 1).

Mineralization in the water column

WCM rates varied between 2.1 and 27.4 mmol O_2 m^{-2} d^{-1}. As a measure of OM mineralization within the hypolimnetic water column, WCM depends on the lakes' volume and

Table 3. Estimation of the water column mineralization rate (WCM) calculated as the difference between AHM and the sum of SOU and F_{red}. TP is the average concentration after winter mixing over the past 10 years. For Lake Brienz, the value of 0.6 mg P m^{-3} is calculated as the bio-available TP (Müller et al. 2006).

Lake	F_{red}	SOU	AHM	WCM	TP
	(mmol O_2 m^{-2} d^{-1})				(mg P m^{-3})
Maggiore	6.0	16.4	26.3	3.9	11.0
Geneva	2.1	8.0	37.5	27.4	24.3
Brienz	1.4	7.9	13.1	3.8	0.6
Constance	2.0	8.6	25.0	14.4	7.5
Thun	2.3	10.6	15.0	2.1	1.8
Lucerne	0.6	11.0	20.3	8.7	4.8
Neuchâtel	3.1	10.6	24.7	11.0	9.8
Walensee	3.6	17.6	20.0	~0	3.2
Aegeri	4.0	11.6	19.7	4.1	5.4
Baldegg	13.8	23.2	42.2	5.2	24.1
Hallwil	5.6	14.8	30.9	10.5	15.8

primary production and thus its TP concentration. Oligotrophic lakes (TP < 10 mg P m^{-3}) that have not experienced eutrophication in the past (Walensee, Lakes Thun, Brienz, and Aegeri) exhibited low WCM values of 2.1 mmol O_2 m^{-2} d^{-1} (Lake Thun) and 4.2 mmol O_2 m^{-2} d^{-1} (Lake Aegeri). WCM could not be estimated from Walensee because the sum of F_{red} (3.6 mmol O_2 m^{-2} d^{-1}) and SOU (17.6 mmol O_2 m^{-2} d^{-1}) already equaled measured AHM (20.0 mmol O_2 m^{-2} d^{-1}; Table 3). Lago Maggiore similarly showed a very low WCM value (3.9 mmol O_2 m^{-2} d^{-1}). Both lakes have exceptionally steep walls which cause substantial sediment focusing leading to elevated SOU and F_{red} at the central coring sites. In the oligotrophic but recovering Lake Constance, WCM values resembled those measured from the mesotrophic Lake Neuchâtel (14.4 and 11.0 mmol O_2 m^{-2} d^{-1}, respectively). The highest WCM rate was observed from the most productive very deep Lake Geneva (27.4 mmol O_2 m^{-2} d^{-1}). The shallower but similarly productive Lakes Baldegg and Hallwil exhibited lower respective WCM rates of 5.2 and 10.5 mmol O_2 m^{-2} d^{-1} (Table 3).

Discussion

Fluxes of reduced substances from the sediment

Very low F_{red} values (< 0.2 mmol O_2 m^{-2} d^{-1}) were previously reported in lakes > 100 m deep such as Lakes Superior (Remsen et al. 1989; Li et al. 2012), Michigan (Thomsen et al. 2004), and Baikal (Och et al. 2012; Torres et al. 2014). These lakes are characterized by low OM accumulation rates and high O_2 penetration depths resulting in prolonged (up to several decades) aerobic mineralization of the settled

OM. Consequently, fluxes of CH_4, NH_4^+, Fe(II) Mn(II) and hence, F_{red}, are close to zero.

The deep lakes investigated by this study (> 100 m) exhibited distinctly higher F_{red} values (average 2.6 ± 1.6 mmol O$_2$ m^{-2} d^{-1}) and showed a consistent dependence on mean lake depth (Fig. 2) (Steinsberger et al. 2017). These were dominated by CH_4 fluxes which constituted up to 99% of F_{red} (Table 2, Fig. 1). NH_4^+ contributions were negligible in all lakes that have never surpassed mesotrophic production in the past. Deeper sedimentary horizons (> 10 cm) however exhibited elevated CH_4 and NH_4^+ concentration of up to 7.0 and 0.6 mmol L^{-1}, respectively. These resembled values measured from river deltas or from shallower, more productive lakes (Sobek et al. 2009; Randlett et al. 2015; Steinsberger et al. 2017). In contrast to the Great Lakes, the deep peri-alpine lakes investigated by this study accumulated inorganic matter from weathering of rocks and OM from their watersheds. This gradually degrading allochthonous OM is diluted with additional mineral deposits resulting in small concentrations of TOC (Supporting Information Fig. S3). High sedimentation rates lead to rapid OM burial in the anoxic sediments. A laboratory study by Grasset et al. (2018) showed that the mineralization of allochthonous OM by methanogenesis, although slower than autochthonous OM degradation, can yield similar overall CH_4 production. This finding helps to explain high pore-water accumulation of CH_4 and NH_4^+ in deeper sediments collected from Walensee and Lago Maggiore.

Consequently, upward diffusing CH_4 and NH_4^+ comes into contact with the main electron acceptors O$_2$, NO_3^-, and SO_4^{2-}, and is (partially) oxidized within the sediment. In consequence, a substantial fraction of O$_2$, NO_3^-, or SO_4^{2-}

consumption could be attributed to F_{red} oxidation rather than by direct aerobic mineralization of OM.

In productive lakes < 100 m deep (Lakes Baldegg and Hallwil), pore-water concentration gradients of CH_4, NH_4^+, Fe(II), and Mn(II) extended to the sediment–water interface. F_{red} attained high rates of 5.6 mmol O$_2$ m^{-2} d^{-1} (Lake Hallwil) and 13.8 mmol O$_2$ m^{-2} d^{-1} (Lake Baldegg) fueled by the high primary production and mineralization of large amounts of TOC deposited during past anoxic periods (Steinsberger et al. 2019).

Sediment oxygen uptake dependence on organic matter

O$_2$ is depleted by the initial aerobic degradation of OM at the sediment surface and by oxidation of reduced compounds produced during anaerobic mineralization within the sediment (Steinsberger et al. 2017). Lakes > 100 m deep exhibited SOU in the narrow 7.9–11.0 mmol O$_2$ m^{-2} d^{-1} range. Walensee and Lago Maggiore exhibited exceptionally high SOU values of 17.6 and 16.4 mmol O$_2$ m^{-2} d^{-1} respectively, which resemble values observed in the shallower and more productive Lakes Hallwil and Baldegg (14.8 and 23.2 mmol O$_2$ m^{-2} d^{-1}; Table 3). The steep slopes of Walensee and Lago Maggiore may increase OM deposition rates by focusing sediment into the central parts of the basin which in turn increases sediment-related O$_2$ consumption. The sediment area relevant for SOU and F_{red} is thus substantially smaller than the hypolimnion area used for AHM estimation. Equation 4 may thus systematically underestimate WCM values for lakes having steep walls.

Sediment-related O$_2$ consumption depends on several key parameters such as bottom water O$_2$ concentrations, O$_2$ penetration depth, TOC mass accumulation rate, and OM susceptibility to mineralization (Polerecky et al. 2006; Sobek et al. 2009; Bryant et al. 2010; Gudasz et al. 2010). All lakes > 100 m deep exhibited sediment TOC contents of 0.5–1.5%, whereas shallower lakes exhibited sediment TOC concentrations of 3.4–3.5% (Supporting Information Fig. S3, Table 4). The more rapid mineralization rates for autochthonous OM relative to the more recalcitrant terrestrial OM (Sobek et al. 2009) suggest that the former is preferentially mineralized in the water column and then deposited mostly as already degraded OM onto the sediment for lakes deeper than 100 m. Schwefel et al. (2018) demonstrated this for the productive Lake Geneva, while Carstens et al. (2013) did so for the oligotrophic Lake Brienz. Consequently, we observed a decreasing trend of SOU with increasing mean lake depths, similar to F_{red} (see Fig. 2).

Elevated TOC concentrations in sediment of lakes < 100 m deep is consistent with the interpretation of limited degradation within the water column and more vigorous O$_2$ consumption in the sediment surface leading to burial of large amounts of partially mineralized OM in sediments.

Table 4 shows that sediment mass accumulation rates in > 100 m deep lakes (Maggiore, Thun, Brienz, and Walensee) unexpectedly resembled or even exceeded that observed from shallower lakes. This reflects elevated areal contributions of allochthonous material from watersheds
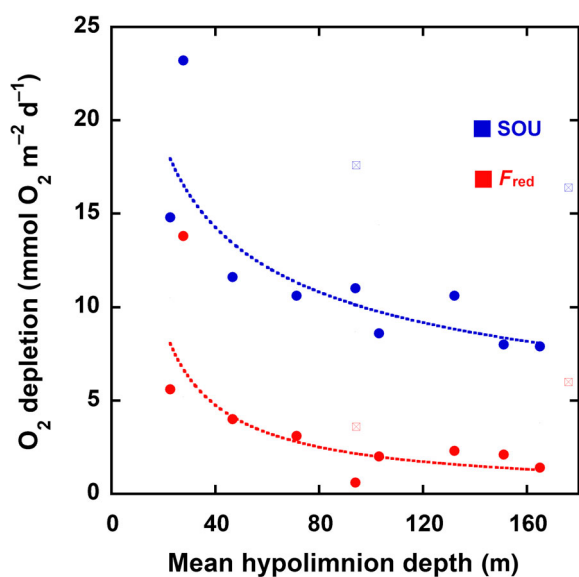
Fig. 2. Depletion rates (mmol O$_2$ m^{-2} d^{-1}) of the sediment-based O$_2$ sinks SOU (blue) and F_{red} (red). SOU and F_{red} decrease with increasing mean hypolimnion depth (see Table 1).

Table 4. Nutrient contents of the bulk sediment. TOC, TN, and TOC-MAR values were averaged over 1–10 cm sediment depth. n.d., not determined. Some data were taken from the respective literature: [1]Frenzel et al. (1990), [2]Span et al. (1990), [3]Schwalb et al. (1998), [4]Müller et al. (2007), [5]Zimmermann (2008), [6]Putyrskaya et al. (2009), [7]Sobek et al. (2009), [8]Wirth et al. (2011), [9]Bierlein et al. (2017),[10]Steinsberger et al. (2017), [11]Schwefel et al. (2018).

Lake	TOC (mg C g^{-1})	TN (mg N g^{-1})	O_2 penetr. depth (mm)	Sed. accumul. rate (mm yr^{-1})	TOC-MAR (g C m^{-2} yr^{-1})
Maggiore	14.9 ± 6.2	1.2 ± 0.6	2.6 ± 0.1	3.4 [6]	33.4
Geneva	11.1 [1]	1.1 [2]	4.0 ± 0.5 [11]	1.0 [10]	11.1
Brienz	5.4 ± 1.4	0.6 ± 0.1	6.3 ± 0.8	6.4 [4]	36.8
Constance	n.d.	n.d.	2.5–4.5 [1,7]	n.d.	n.d.
Thun	11.3 ± 2.0	1.2 ± 0.2	4.8 ± 0.2	6.8 [8]	67.7
Lucerne	n.d.	n.d.	4.8 ± 0.6	n.d.	n.d.
Neuchâtel	22.4 ± 0.8	2.5 ± 0.4	3.6 ± 0.4	2.5 [3]	23.9
Walensee	11.3 ± 1.8	1.3 ± 0.1	5.3	5.7 [5]	42.9
Aegeri	34.9	3.6 ± 0.7	2.5 ± 0.7	1.9 [10]	22.8
Baldegg	34.2 ± 3.1	3.9 ± 0.4	3.4 ± 0.8	3.3 [10]	45.6
Hallwil	34.4 ± 3.5	4.0 ± 0.2	3.0 ± 1.0 [9]	2.0 [10]	22.5

(Wirth et al. 2011; Thevenon et al. 2013) as well as sediment focusing by funnel- or trench-shaped lake basins (Lehman 1975; Blais and Kalff 1995). The exposure time of OM to O_2 falls well below 1 year. Combined with elevated MAR, these conditions bury significant amounts of OM in anoxic sediment before degradation can occur. The elevated TOC-MAR lead to anaerobic mineralization in the deeper sediment which then generates CH_4 and NH_4^+ observed at high concentrations in the sediment pore water. These species can delay lake recovery from eutrophication with respect to O_2 concentrations. However, all of the Fe(II) and Mn(II) and most of the NH_4^+ are oxidized within the sediment. These do not reach the sediment–water interface and thereby increase SOU (Supplementary Fig. S1).

The range of SOU determined from lakes > 100 m deep investigated here (11.3 ± 3.7 mmol O_2 m^{-2} d^{-1}) is consistent with fluxes reported by literature sources for other large and deep lakes. Thomsen et al. (2004) reported a SOU rate of 7.7 ± 2.1 mmol O_2 m^{-2} d^{-1} for Lake Michigan while Li et al. (2012) reported a SOU rate of 6.1 ± 1.4 mmol O_2 m^{-2} d^{-1} for Lake Superior. Lower SOU values were reported for the ultra-deep oligotrophic Lake Baikal. These include an overall value of 3.3 ± 1.1 mmol O_2 m^{-2} d^{-1} (Müller et al. 2005), 1.4 to 5.6 mmol O_2 m^{-2} d^{-1} for the South Basin (Och et al. 2012), and 1.1 mmol O_2 m^{-2} d^{-1} for the North Basin (Martin et al. 1998). O_2 penetration depths determined for the deep lakes analyzed here (2.6–6.3 mm, Table 4) resembled values previously reported for Lake Constance (1.5–6.3 mm; Frenzel et al. 1990; Sobek et al. 2009) but were distinctly lower than those reported for Lakes Michigan (21 ± 2.5 mm), Superior (40–110 mm), and Baikal (20–44 mm). This evidences the high consumption of O_2 within the first millimeters of sediment rendering O_2 penetration depths more similar to those in the fully productive and shallower Lake Baldegg

(0.9–2.0 mm). Lakes Michigan and Superior exhibit low SOU rates and corresponding higher O_2 penetration depths that result from low OM sedimentation rates, intense bioturbation and extensive Fe cycling with only small NH_4^+ and insignificant CH_4 production. For lakes analyzed in this study, excess O_2 that could reach deeper parts of the sediment due to the absence of reactive OM is apparently consumed by a front of upward diffusing reduced compounds produced by anaerobic mineralization of OM. Decreasing pore-water concentrations of reduced species in the uppermost layers of sediment reported here offer further evidence of rapid anaerobic turnover (Maerki et al. 2006).

Fluxes of NO_3^- into the sediment indicating mineralization of OM by denitrification ranged from 0.32 to 2.36 mmol O_2 m^{-2} d^{-1} and thereby only a small fraction of total SOU (between 2.9% in Lago Maggiore and 12.5% in Lake Lucerne). Li et al. (2012) and Thomsen et al. (2004) report similarly low estimates for Lakes Superior and Michigan (< 5%). Overall NO_3^- removal rates (coupled nitrification–denitrification) however may be higher due to a hidden contribution from anaerobic NH_4^+ oxidation with low concentrations but high turnover rates of NO_3^-/NO_2^- to N_2 (e.g., anammox; Small et al. 2013; Crowe et al. 2017). In fact, at least in five of the lakes investigated here (Walensee, Neuchâtel, Thun, Brienz, and Lucerne), a rapid decline in NH_4^+ concentrations (with NH_4^+ consumption rates of 0.08–0.46 mmol m^{-2} d^{-1}) well below the O_2 penetration depth was evident. These conditions clearly indicate anaerobic NH_4^+ oxidation (Zhu et al. 2013). As NO_3^- penetrates deeper into the sediment than O_2 (5 mm – 45 mm), anammox bacteria might be actively oxidizing NH_4^+ (Wenk et al. 2013).

Fluxes of SO_4^{2-} ranged from 0.32 to 2.70 mmol O_2 m^{-2} d^{-1} (average 1.19 mmol O_2 m^{-2} d^{-1}), and were well within the range of SO_4^{2-} reduction rates given by Holmer and

Storkholm (2001). In general, SO_4^{2-} fluxes contributed ~ 11% to SOU, while in Lake Geneva and Lake Thun, due to high loads from the catchment geology, SO_4^{2-} fluxes contributed about one third to SOU. The full extent of SO_4^{2-} reduction induced by OM mineralization is likely masked by (cryptic) internal sulfide re-oxidation and sulfite complexation processes (Holmkvist et al. 2011). Hence, SO_4^{2-} fluxes likely underestimate actual SO_4^{2-} reduction rates.

Mineralization in the water column

In the hypolimnetic water column, OM is mineralized by a large variety of microbes that consume O_2 (Carstens et al. 2012). Subsequent O_2 consuming processes at the sediment–water interface depend on excess OM passing through the water column. Therefore, depending on the main mineralization sites of OM (hypolimnetic water, sediment surface, deep sediment) lakes show characteristic patterns in the three O_2 sinks (WCM, SOU, and F_{red}).

Livingstone and Imboden (1996) proposed that WCM represents a significant proportion of AHM for large lakes with a high mean hypolimnion depth. This is true for productive lakes such as Geneva (77%) and Neuchâtel (45%) and lakes recovering from a eutrophic phase, such as Lakes Constance (58%) and Lucerne (43%) (Table 3, Fig. 3). This is in agreement with the modeled WCM value of Lake Geneva by Schwefel et al. (2018). However, lakes that never experienced high productivity periods, such as the oligotrophic Lakes Brienz, Thun, and Walensee, did not show elevated WCM rates. These lakes instead showed WCM contributions to AHM of

only ~ 14%, ~ 29% and ~ 0%, respectively. They also exhibited low sediment TOC content but a high rate of sediment OM accumulation caused by high loads of allochthonous particles (Finger et al. 2007; Bechtel and Schubert 2009). These lakes also mineralize a relatively small amount of OM within the hypolimnetic water column compared to that deposited at the sediment surface (Fig. 3). The high SOU and F_{red} rates indicate mineralization of allochthonous OM. The very low WCM of Walensee and Lago Maggiore reflect high SOU and F_{red} caused by sediment focusing (Blais and Kalff 1995). Lake Baldegg exhibited WCM of only 5.2 mmol O_2 m^{-2} d^{-1} or 12% of AHM. This likely reflects the shallower lake depth and brief mineralization window for settling autochthonous OM.

WCM primarily depends on the export of autochthonous OM from the productive zone to the hypolimnion. Because it originates from primary production, it must be therefore related to TP for concentration ranges where TP availability influences primary production. In order to compare WCM between lakes of different depths, we normalized WCM to the mean hypolimnion depth, z_H to obtain a relationship with TP (Fig. 4). In all non-aerated lakes, WCM increases in proportion to TP. For a TP range of 10–15 mg P m^{-3}, WCM levels off indicating that additional TP exerts limited influence on primary production and thus on OM export to the hypolimnion and subsequent O_2 consumption. Below a TP concentration of ~ 10 mg P m^{-3}, WCM covaries closely with TP concentration. This is in line with the observation of Müller et al. (2019) that AHM in seasonally stratified lakes increases approximately in proportion to the areal amount of bio-available P but levels off above this threshold value. O_2 consumption in lakes > 100 m deep may immediately respond to a decrease of TP for concentrations below this threshold. Decreasing TP concentration in Lake Geneva by half could initiate a substantial reduction in WCM, the lake's primary O_2 sink. By contrast, minor interventions to reduce TP levels for Lakes
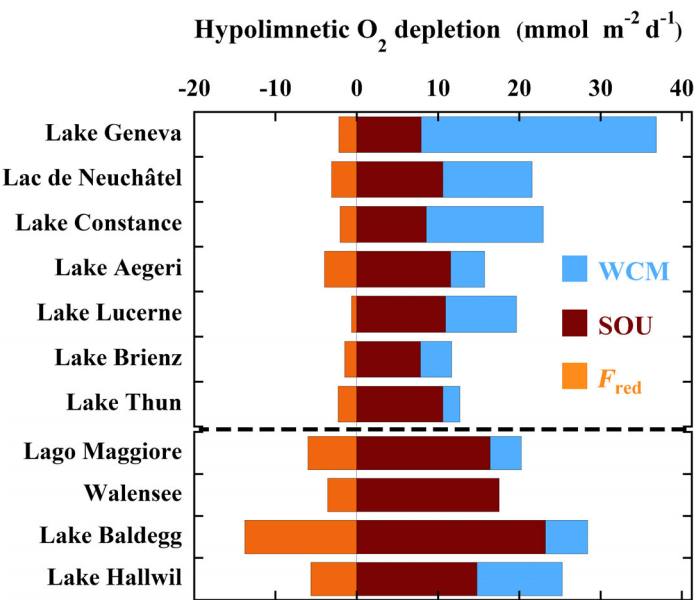
Fig. 3. Hypolimnetic O_2 consumption itemized to the three O_2 sinks: F_{red}, SOU, and WCM. Lakes are divided into two groups: very deep lakes (above dashed line), lakes biased by intense sediment focusing which causes increased SOU and F_{red} (Lago Maggiore and Walensee) and artificially aerated deep Lakes Baldegg and Hallwil (below dashed line).
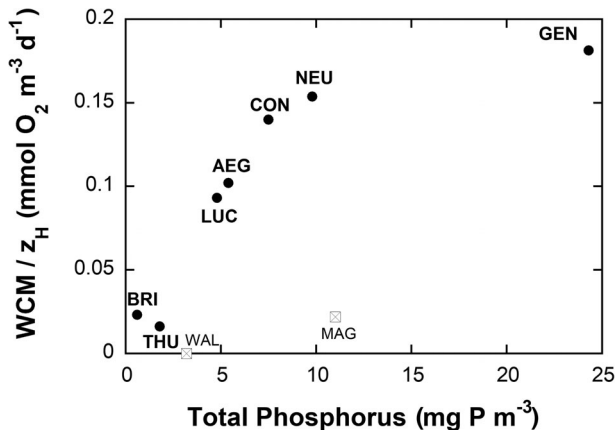
Fig. 4. Oxygen consumption rates for the water column (WCM) normalized by mean hypolimnion depth (z_H). WCM increases with TP up to a value of around ~ 10 mg P m^{-3} and then levels off. Lakes Baldegg and Hallwil are not shown because they are artificially aerated.

Neuchâtel and Constance would readily influence WCM and thereby decrease total AHM.

Conclusion

Diffusive fluxes of reduced substances from and flux of O$_2$ into the sediments were measured in lakes with depths ranging from 48 to 372 m. Areal hypolimnetic mineralization rates were calculated from (monthly) O$_2$ monitoring data and used to estimate the water column mineralization rates. This analysis showed that:

- Despite high O$_2$ concentrations (> 190 μmol O$_2$ L^{-1}) in bottom waters of all lakes, O$_2$ penetrated sediments only to depths of 2.6 to 6.3 mm resulting in high O$_2$ fluxes. In lakes deeper than 100 m, reduced substances from anaerobic mineralization of OM in the sediment constituted a major fraction of the sediment oxygen uptake and prevent O$_2$ from penetrating deeper into the sediment.
- Most lakes deeper than 100 m exhibited similar levels of sediment O$_2$ consumption by SOU and F_{red}. This suggests that OM deposited at the sediment surface was already largely mineralized. The O$_2$ reservoir of the more extensive hypolimnia sufficed to degrade most of the settling OM. Hence, SOU and F_{red} values did not depend on trophic state for lakes deeper than 100 m.
- WCM represented a major contribution to AHM in lakes of > 100 m depth. This contribution decreased with TP when less autochthonous OM was available for O$_2$ consumption. WCM increased with increasing TP concentrations until a threshold of 10–15 mg P m^{-3} was reached. Above this threshold, WCM leveled off. Reducing TP concentrations in productive lakes deeper than 100 m to below this threshold could therefore exert a strong influence on AHM.

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Conflict of Interest

None declared.