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Key Points:

- The export of organic carbon from the productive surface zone of lakes to the deep water was estimated from the consumption of oxygen and the net deposition in the sediment
- Interference from terrestrial organic carbon or changing trophic can be compensated by subtracting the flux of reduced substances diffusing from the sediment
- Estimated net export rates were in agreement with sediment trap measurements and seasonal export of phosphorus and nitrogen from the productive surface layer

Supporting Information:

Supporting Information may be found in the online version of this article.

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Net Ecosystem Production of Lakes Estimated From Hypolimnetic Organic Carbon Sinks

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Abstract This study presents a novel concept for estimating net ecosystem production (NEP), the export of organic carbon (OC) from the productive surface layer to the deep-water (hypolimnion) of 11 seasonally stratified lakes, varying in depth and trophic state. As oxygen remineralizes settling OC at a constant ratio, NEP is equivalent to the areal hypolimnetic mineralization rate (AHM) plus burial in the sediment. Two major interferences have to be considered, however. First, OC from terrestrial sources, not originating from primary production, consumes a fraction of oxidants. Second, sediment diagenetic processes of lakes in trophic transition (e.g., undergoing eutrophication or reoligotrophication) that are not in quasi-steady-state with actual fluxes of OC from the productive surface layer, bias the NEP estimation. In these cases, the flux of reduced substances diffusing from the sediment must be subtracted. This results in some overestimation for lakes with high allochthonous loads, and slight underestimation in lakes that are not in quasi-steady-state, because the actual sediment burial of autochthonous OC is small but not negligible. The presented approach requires data from routinely available monitoring and thus can be applied to historic data. The temporal integration over the productive season makes the estimation of NEP robust. Based on a historic 47 years long data record of Lake Geneva, NEP estimations ($\sim 70 \text{ gC m}^{-2}$) from AHM rates agree well with P and N export budgets from the productive surface zone, which help to verify and constrain the uncertainty of the estimates.

Plain Language Summary The organic matter that is produced in the surface layers of lakes and subsequently settles to the deep water drives the consumption of oxygen and thus the source of reducing conditions with its adverse consequences for sediment quality, drinking water treatment, and the oxygen-dependent fauna. The determination of its flux rate is very laborious and prone to large inaccuracy. We present a novel concept that allows simple estimation of the flux of organic matter, based on monitoring data of oxygen and net sedimentation. In the ideal case, this organic matter flux directly corresponds to the sum of oxygen consumed in the deep water plus the organic carbon deposited in the sediment. Two major interferences can occur that require special consideration. First, organic carbon from terrestrial sources, not originating from primary production, consumes also oxidants. Second, sediment formation of lakes in transition from nutrient-poor to nutrient-rich or vice versa, are not in quasi-steady-state with actual fluxes of organic carbon in the productive surface layer, and thus bias the estimation of the carbon flux. This can be amended when the flux of reduced substances diffusing from the sediment is taken into account.

1. Introduction

Primary production in the photic surface layer is at the onset of life and the trophic cascade in natural waters. The assimilation of carbon (C), phosphorus (P), nitrogen (N) and other nutrients as well as the release of oxygen (O_2) in the productive surface zone is reversed in the hypolimnion as organic particles settle through the water column to the sediment surface (Wetzel, 2001). If this cycling is excessive, the well-known adverse effects of deep-water anoxia, accumulation of large amounts of deposited organic carbon (OC) and the release of reduced substances (methane, ammonium) from the sediment is observed. The flux of OC leaving the productive surface layer and settling across the density (temperature) gradient into the hypolimnion is termed *net ecosystem production* (NEP, in units of $\text{gC m}^{-2} \text{ yr}^{-1}$). In the productive zone, primary production and respiration occur simultaneously with diurnally changing intensities. Primary production takes place during daylight, whereas respiration is active during the entire day. Both processes are

temporally variable depending on light intensity and predominating plankton species among other parameters, resulting in a variability of NEP, which is calculated as primary production minus respiration. Determination of primary production is laborious and forming averages based on a few profile estimates per year leads to large uncertainty for this strongly varying process. Therefore, NEP is the preferred reference to quantify the trophic level of lakes (Wetzel, 2001). It controls the consumption of O_2 and thus the source of reducing conditions in the hypolimnion with its adverse consequences for sediment diagenesis, drinking water treatment, and the O_2 -dependent fauna. The estimation of NEP as an integrated value for the whole duration of the productive (summer) period is often measured with sediment traps positioned directly below the trophic surface zone of the lake.

The rate of change of the O_2 concentration in the free water using in situ sensors in day-night cycles provides direct access to primary production and community respiration (Giling et al., 2017; Obrador et al., 2014; Staehr et al., 2012). This so-called diel O_2 technique, using high temporal resolution sensors, allows versatile applications from moorings (Marcé et al., 2016) or remotely controlled vehicles (Briggs et al., 2018). In a recent study on Lake Geneva, Fernández-Castro et al. (2021) quantified metabolic rates with an autonomously profiling multi-parameter probe and from mooring measurements over the top 30 m during the productive season. The separation of the metabolic from physical processes such as water-atmosphere exchange, lake internal baroclinic motions, and turbulent diffusive downward transport, however, complicates the simple idea and requires additional data on gas exchange and diffusion coefficients.

An alternative approach for the estimation of NEP is the quantification of the sinks of OC in the hypolimnion instead of the sources of OC in the productive zone. The mineralization of OC takes place in three distinct realms of the hypolimnion, which involves three measurable sinks for O_2 : (1) while settling through the water column (water column mineralization, WCM; Schwefel et al., 2018), (2) oxic mineralization of the freshly deposited OC at the sediment surface (sediment oxygen uptake, SOU; Steinsberger, Schwefel, et al., 2020), and (3) oxidation of reduced substances produced by anaerobic sediment diagenesis and diffusing out of the sediment into the supernatant lake water (RED; Steinsberger, Schmid, et al., 2017).

As the hypolimnetic O_2 depletion is driven by primary production, previous studies focused on linking lake P concentrations to this OC source and thereby to hypolimnetic O_2 depletion (Hargrave, 1972). Charlton (1980) hypothesized that in very deep lakes almost all OC derived from primary production was mineralized within the hypolimnetic water column (WCM), if its depth was large enough, with only a small fraction being mineralized at the sediment-water interface (SOU). Several studies showed that in deep lakes, independent of whether they are oligotrophic or eutrophic, such as Lakes Baikal (Maerki, Müller, & Wehrli, 2006), Superior (J. Li et al., 2012) or Geneva (Schwefel et al., 2018), SOU and RED were low (Torres, Och, et al., 2014), and NEP was mineralized almost entirely within the long hypolimnetic water columns (WCM). Only a small fraction of OC was buried in the sediments (NS). Hence, in very deep lakes, the areal hypolimnetic O_2 consumption (AHM) plus NS is a direct measure of NEP.

In productive lakes with a mean hypolimnion depth smaller than ~40 m (Müller, Steinsberger, Schwefel, et al., 2019), O_2 is often exhausted in the hypolimnion due to the settling OC, and considerable amounts of partly mineralized OC can be buried in the sediments. This so-called “*sediment carbon legacy*” (Carey et al., 2018) or “*sediment memory effect*” (Matzinger et al., 2010) is the reason for increased SOU and the production of RED diffusing upwards from deeper sediment layers (Steinsberger, Schwefel, et al., 2020). It provokes a continued high O_2 consumption in the hypolimnia of lakes in spite of a possible earlier amelioration of P loads. The remaining refractory OC, escaping early diagenetic mineralization due to anoxic conditions, is eventually buried in the sediment. The origin of sediment OC can potentially be a mix from two sources, primary production within the lake (autochthonous), and terrestrial material riverine-flushed from its catchments (allochthonous).

Here we present the estimation of NEP by balancing the key constituents in the receiving stratified water volume immediately below the productive zone. As the mineralization of OC corresponds to the depletion of O_2 in the hypolimnion, NEP can be calculated from the sum of O_2 (and other oxidants) consumed in the hypolimnion, reduced compounds accumulation (such as from settled OC and fluxes of methane, ammonium and other reduced substances from the sediment), and the NS of OC. Whenever possible, we also compared these NEP values with estimates based on sediment trap measurements. An additional way of NEP



Figure 1. Map of Switzerland with the 11 lakes included in this study (Table 1).

estimation uses nutrient balances of the epilimnion. NEP must be related to the quantity of the essential nutrients P and N removed from the trophic surface zone during the productive season. C, P and N are taken up in distinct ratios (Redfield et al., 1963) albeit variability is large (Hecky et al., 1993; Sterner et al., 2008) and depends on the trophic state of lakes (Müller, Steinsberger, Schwefel, et al., 2019). NEP quantification requires therefore not only the seasonal budgets of the essential nutrients P and N in the epilimnion, comprising internal and external load and export, but also the elemental ratios (C:P and/or C:N) of particulate settling OC (Müller, Steinsberger, & Wüest, 2021). We established seasonal epilimnion budgets of P and N as an alternative way of NEP estimation that allowed crosschecking and assessment of plausibility and consistency of the O_2 -based approach.

2. Methods

2.1. Sampling and Analysis

Eleven medium to large lakes in Switzerland were included in this study (Figure 1; Table 1). In each lake investigated, four sediment cores were taken, usually at the deepest location of the lake. Individual sediment cores were collected for porewater analysis including CH_4 sampling, for O_2 microprofile measurements at the sediment surface and for bulk sediment analysis of total OC (TOC), P, and N. Coring was performed using a gravity corer with 60 cm long PVC liners (6 cm diameter) with predrilled and taped holes for sediment porewater and CH_4 sampling (Torres, Hauser, et al., 2013).

For CH_4 sampling, syringes with clipped tips were used to extract 2 cm³ of sediment aliquots by punching through the horizontally staggered and taped holes of 1.2 cm diameter in the liner at 1 cm intervals. Aliquots were directly transferred into glass flasks of known volume containing 2 mL of 7 M NaOH, capped,

Table 1
The Eleven Lakes Considered in This Study Sorted According to Maximum Depth

Lake	Volume (km ³)	Area (km ²)	Depth (m)	z_H (m)	TP _{mix} (mg m ⁻³)	AHM (gO ₂ m ⁻² d ⁻¹)	Time period
Maggiore	37.6	213	371	176	12	0.84 ± 0.17	1988–2018
Geneva	89.1	582	309	151	18	1.25 ± 0.18	1966–2019
Brienzen	5.02	29.8	259	165	3.4	0.54 ± 0.05	2011–2020
Constance ^a	47.8	473	253	103	7.5	0.81 ± 0.05	1994–2016
Thun	6.46	47.9	214	132	2.9	0.62 ± 0.09	2000–2020
Neuchâtel	13.8	218	153	71	11	0.69 ± 0.12	2010–2019
Lucerne ^b	2.30	22.0	151	94	4.4	0.35 ± 0.11	2005–2019
Walensee	2.52	24.1	151	95	3.4	0.60 ± 0.16	2007–2017
Aegeri	0.35	7.3	81	40	6.0	0.60 ± 0.11	2000–2018
Baldegger	0.17	5.2	65	25	22	1.27 ± 0.22	2000–2019
Hallwil	0.29	10.0	46	19	13	0.81 ± 0.02	2016–2019

Note. Values for areal hypolimnetic mineralization rates (AHM) were estimated assuming an epilimnion depth of 15 m. z_H is the mean hypolimnion depth (below 15 m). TP_{mix} concentrations were averaged for the last five years of the time period listed.

^aUpper Lake Constance. ^bVitznau Basin, a sub-basin of Lake Lucerne.

stored at 4°C in the dark and analyzed from the headspace with an Agilent GC using a Supelco Carboxene 1010 column.

Sediment porewater was sampled in vertical resolutions of 5 mm in the top 5 cm, of 1 cm in the subsequent 5 cm and finally of 2 cm until 20 cm depth. Extraction was performed with Micro Rhizon® filter tubes (1.5 mm diameter, Rhizosphere Research Products, Wageningen, Netherlands) by punching through the taped 2 mm holes. Volumes of 10–50 µL of sediment porewater were extracted, transferred to 200 µL flip tubes and directly injected into a capillary electrophoresis CE-C⁴D device allowing on-site measurements (Steinsberger, Schmid, et al., 2017; Torres, Hauser, et al., 2013). Two CE-C⁴D devices (anions and cations) were calibrated on-site with multi-cation calibration standards from Fluka and multi-anion standards from Roth. Standard deviations of all calibrations were well below 5%.

Oxygen concentrations of the sediment-overlying water were determined using the standard Winkler method (GSM, 2002). Vertical O₂ concentration profiles were recorded with a PreSens O₂ micro-optode mounted to an automated micromanipulator. The optode had a flat tip size of 230 µm, a detection limit of 0.64 µmol O₂ L⁻¹ and a response time of <10 s. O₂ concentration was measured in the range between 2 cm above and 3 cm below the sediment-water interface at 100 µm vertical intervals and a downward speed of 100 µm s⁻¹, stopping for each measurement.

Sediment cores used for bulk analysis were stored in a cold room at 4°C until processing. The cores were sampled in 0.5 cm sections in the top 10 cm and in 1 cm sections from 10 cm downward, weighed and freeze-dried. Water content was calculated from the weight difference before and after freeze-drying. Sediment porosity was estimated from water content, sediment density and TOC content (Och et al., 2012). After grinding, the sediment samples were further analyzed for total carbon (TC) and total nitrogen (TN) with a Euro EA 3000 (HEKAtech). Total inorganic carbon (TIC) was determined with a Coulometer (CM5015 UIC), and TOC was calculated by difference between TC and TIC. Total phosphorus (TP) was photometrically determined with the molybdenum blue method after oxidative digestion with potassium persulfate (K₂S₂O₈) in an autoclave (DEV, 2002). Mass accumulation rates of TOC, P and N (mg m⁻² yr⁻¹) were calculated from bulk NS rates obtained from ¹³⁷Cs and ²¹⁰Pb dating. To achieve comparable units in reference to NEP, which is calculated over half a year (productive summer period; gC m⁻² (180 days)⁻¹), sediment core and sediment trap data were also calculated into the same time frame (gC m⁻² (180 days)⁻¹). We suggest using the time interval of 180 days as this is close to the average duration of lake stratification on the Swiss Plateau and makes data comparable to other lakes.

The average time span of lake stratification varies, among others, depending on bathymetry, altitude, wind exposition, winter temperatures and has been observed to increase with climate warming (Råman Vinnå et al., 2021). Characteristic process rates, however, remain almost unaffected when normalized to 180 days, and mass conversions can be adjusted to the respective stratification duration of each individual lake. This implies that also NS resulting from dated sediment cores must be halved, which may cause slight underestimation because the settling rate of particulate matter is higher during the stratified than during the (winter) mixing season. Moreover, we implicitly disregard the fraction of sediment OC mineralized during the mixing season. As no quantitative information is available to compensate for this fraction, NEP may be slightly underestimated. However, we think that this approach is the best option also in view of the inherently large inaccuracies that originate from determination of the sedimentation rates from dated cores.

Local heterogeneities in sediment deposition could not be characterized. However, locations for sediment core retrievals were carefully selected to prevent bias by river inputs, delta depositions or turbidites from lake internal sediment slides.

2.2. Calculation of Porewater Fluxes

Diffusive sediment porewater fluxes J ($\text{mmol m}^{-2} \text{d}^{-1}$) of O_2 , CH_4 , NH_4^+ , Mn(II) , and Fe(II) were calculated from vertical concentration gradients (Equation 1). Free sulfide (S(-II)) was not detected in any of the porewater samples, which is explained by the presence of free Fe(II) . The one-dimensional steady-state diffusion-reaction model by Epping and Helder (1997) was adapted to fit the porewater gradients and to extract the fluxes of the compounds (Müller, Wang, et al., 2003). Temperature-corrected (4°C) diffusion coefficients from Y. H. Li and Gregory (1974) and porosity-corrected formation factors ($1.02 \times \text{porosity}^{-1.81}$) for clay-silt sediment (Maerki, Wehrli, et al., 2004) were used. Based on the redox stoichiometry, the estimated fluxes of reduced substances (RED: CH_4 , NH_4^+ , Mn(II) , and Fe(II)) were converted to O_2 equivalent fluxes (32 g mol^{-1}) by using

$$\text{RED} \left[\text{gO}_2 \text{ m}^{-2} \text{ d}^{-1} \right] = \left(2 \times J_{\text{CH}_4} + 2 \times J_{\text{NH}_4} + 0.5 \times J_{\text{Mn(II)}} + 0.25 \times J_{\text{Fe(II)}} \right) \times 32 \quad (1)$$

2.3. Estimation of Areal Hypolimnetic Mineralization Rates

The areal hypolimnetic mineralization rates (AHM) of Lake Geneva were calculated using the concentrations of O_2 , CH_4 , NH_4^+ , and NO_2^- of the biweekly to monthly CIPEL monitoring data and the lake bathymetry (CIPEL: *Commission Internationale pour la Protection des Eaux du Léman*). Monitoring data sets for other lakes were provided by several Cantonal Authorities and the Swiss Federal Office for the Environment (FOEN). The difference between the maximum O_2 content after winter mixing (usually March to April) and minimum content (October to November) in the hypolimnion below 15 m depth was normalized to the hypolimnion area at 15 m depth and time difference to obtain AHM [$\text{gO}_2 \text{ m}^{-2} \text{ d}^{-1}$] for each productive season (Matzinger et al., 2010; Müller, Bryant, et al., 2012). In most lakes, primary production is confined to the epilimnion above the temperature gradient. In very clear lakes, where the photic depth reaches down into the hypolimnion, the depth for the calculation of the O_2 balance (AHM) must be appropriately adapted. AHM estimates for all lakes included in this study were available for many decades, however in case of decreasing trends due to oligotrophication, only averages of the most recent years were considered for the estimation of NEP (Details in Table SI-1).

Additional sediment diagenetic processes such as denitrification and the reduction of SO_4^{2-} , Fe(III) , and Mn(IV) contribute to post-depositional OC mineralization (Maerki, Müller, Dinkel, & Wehrli, 2009). Their contribution however is only a few % and is neglected for the sake of simplicity but is shown in the supporting information.

2.4. Nutrient Mass Balance in the Productive Surface Layer

Net ecosystem production of a lake can also be expressed by the net removal of P and N from the trophic surface layer during the productive season. The balance of P and N for the surface layer is:

$$P_{NEP} = P_{Spring} - P_{Fall} + P_{in} - P_{out} \quad (2)$$

$$N_{NEP} = N_{Spring} - N_{Fall} + N_{in} - N_{out} \quad (3)$$

P_{Spring} , P_{Fall} , and N_{Spring} , N_{Fall} are the stock amounts of TP and TN present in the surface layer in spring and fall. They were estimated from the monitoring profiles data of CIPEL for the top 30 m at the deepest site of Lake Geneva (SHL2, SwissGrid 534.700/144.950). Volume-weighted average TP and TN contents were calculated as the difference between volume-weighted averages at the end of winter mixing (average of February to April) and at the end of summer stratification (average of September and October). The mean stratification time (Δt) was set to 180 days. P_{in} and N_{in} are the loads introduced by tributaries and atmosphere during these 180 day periods of the productive season considered, and P_{out} and N_{out} express the export via outflow (detailed comments in Section SI-1). Water discharge and nutrient concentrations (DIP, TP and TN) of the largest tributaries to Lake Geneva, the rivers Rhône, Dranse, Aubonne, and Venoge, were available since 1970 from the annual reports of CIPEL (2020). Data analysis details are provided in Section SI-1. The export loads of TP and TN were estimated from the daily water outflow at the gauge station at Geneva-Halle, and interpolated TP and TN concentrations (averages of 0 and 5 m depth) from the monthly monitoring of the Petit Lac (western basin of Lake Geneva, station GE3, SwissGrid 506.069/128.073). Finally, the estimation of NEP in carbon equivalents ($\text{gC m}^{-2} (180 \text{ days})^{-1}$) required the molecular ratio of C:P and C:N of the particulate matter. We used the CIPEL (2020) monitoring data of particulate P, particulate N and particulate OC over the productive layer thickness as defined above. Those balances in the productive surface layer provide nutrient-based NEP estimates, which serve as cross-check for plausibility of the estimates determined with the O_2 -based method.

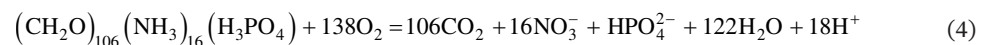
2.5. Gross Primary Production in Lake Geneva

Gross primary production in Lake Geneva was estimated from the CIPEL measurements (^{14}C assimilation method) using the software SoftLake (Cannata et al., 2020; Franchini et al., 2017; C. Minaudo, pers. comm.) to integrate the cumulative production over the entire season. The model performs interpolation between measured ^{14}C assimilation profiles using production-irradiance curves based on chlorophyll profiles and continuous PAR data. The resulting hourly production values are finally integrated over depth and time (units: $\text{gC m}^{-2} (180 \text{ days})^{-1}$).

3. Analysis Approach

3.1. Estimation of Net Ecosystem Production

We propose and validate a novel procedure for estimating NEP of lakes. Instead of measuring the export rate of OC from the productive zone, we suggest determination of NEP from the sinks of OC in the hypolimnion, i.e., consumption of O_2 and deposition in the sediments. The molecular ratio of C: O_2 for the mineralization of OC with O_2 is given by the equation for production and mineralization (Stumm & Morgan, 1996):



The ratio for C: O_2 of 106:138 is nearly independent of the content of N and P in the organic matter. The subsequent description of the procedure to estimate NEP for various lake types is also given in Table SI-1. Oxygen consumption processes are illustrated in Figure 2.

3.2. Net Ecosystem Production in Lakes Dominated by Autochthonous Organic Matter

When lakes with mainly autochthonous OC are in quasi-steady-state with respect to the P budget (no oligotrophication nor eutrophication), settling OC is either mineralized or buried in the sediment. Emerging reduced compounds from anoxic sediment diagenesis or anoxic bottom waters are oxidized in the oxic part of the hypolimnion. For deep lakes ($z_H > 40 \text{ m}$, right in Figure 2), it has been shown that the autochthonous OC production is almost entirely mineralized within the water column during settling (Schwefel

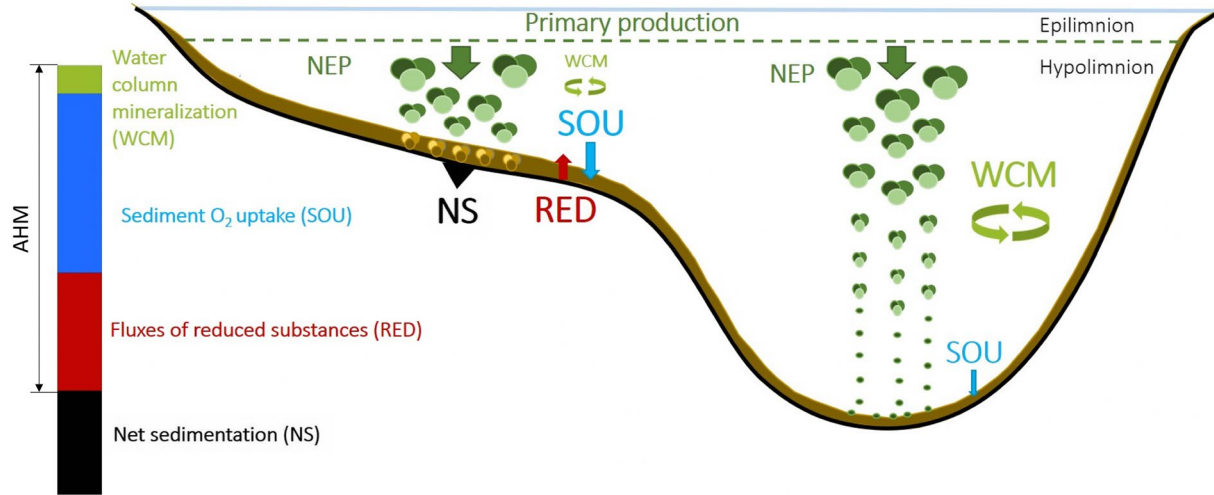


Figure 2. Schematic illustration of NEP in lakes with $z_H < 40$ m (left side) and deep lakes (right side). In lakes with $z_H \leq 40$ m (max depth ≤ 100 m) only a portion of NEP is mineralized in the water column (WCM). Parts of NEP are deposited at the sediment surface and cause O_2 uptake (SOU) at the sediment-water interface. If anoxic conditions occur, a higher fraction of OC is consequently buried within the sediments (NS), generating the slowly upward diffusion of reduced substances in the deeper parts of the sediments (RED). In deep lakes ($z_H \geq 40$ m; max depth ≥ 100 m) with oxic bottom water, NEP is predominantly mineralized within the hypolimnetic water column (WCM) and at the sediment surface (SOU). A detailed description is given in Table SI-1.

et al., 2018). This results in small fluxes of RED and permanent oxic conditions in the water immediately overlying the sediment. Therefore, NEP corresponds to the sum of AHM and NS by:

$$NEP \left[gC m^{-2} (180 \text{ days})^{-1} \right] = (AHM + NS) \times (106 / 138) \times (12 / 31) \times 180 \text{ days} \quad (5)$$

AHM and NS have units of $[gO_2 m^{-2} d^{-1}]$, whereas NEP is expressed per season (180 days) and has units of $[gC m^{-2} (180 \text{ days})^{-1}]$. The right part of Figure 2 conceptually illustrates the fate of C and O_2 in the hypolimnion.

When lakes recover from eutrophication, their sediments – especially in lakes with $z_H < 40$ m – may be loaded with refractory OC from the past generating a contribution of RED that is disconnected from contemporary NEP and should be subtracted from the actual AHM estimate.

$$NEP \left[gC m^{-2} (180 \text{ days})^{-1} \right] = (AHM - RED + NS) \times (106 / 138) \times (12 / 31) \times 180 \text{ days} \quad (6)$$

This setting is depicted in the left part of Figure 2. This approach, on the one hand, leads to a slight underestimation of NEP, because the fluxes of RED in oligotrophic lakes are still not entirely negligible. On the other hand, NS decreased with oligotrophication, which is however, based on practical experience, difficult to determine due to insufficient accuracy of sediment dating in the uppermost zone. Both effects combined might alleviate the overall error. The above arguments also apply for lakes with anoxic bottom waters, because reduced compounds released to or generated within an anoxic hypolimnion are included in AHM. Hence, for steady-state situations, NEP equals AHM plus NS (Equation 5), while for oligotrophicating lakes, Equation 6 applies. For eutrophicating lakes, NS is increasing, and so is RED. Those sediment parameters are not in steady-state with the developing trophic situation and, therefore, the concept is not or only poorly applicable.

3.3. Net Ecosystem Production in Lakes With High Allochthonous Inputs

Loads of terrestrial (allochthonous) OC imported to the lake from its catchment cause consumption of oxidants additional to that consumed by autochthonous production. Allochthonous OC is degraded with

a much smaller rate than planktonic carbon from autochthonous production (Grasset et al., 2018). The contribution to O_2 consumption in the water column (WCM) may therefore be negligible compared with that from autochthonous OC, and we assume that the major fraction of this material is deposited in the sediment where it is accumulated. OC degradation in the sediment, although slow, can produce high fluxes of RED and thus consume a substantial fraction of O_2 of the hypolimnion, especially in deep or oligotrophic lakes. This allochthonous fraction in the sediment, and therefore the corresponding additional flux of RED, is not part of NEP and thus must be excluded in the NEP estimation. For deep lakes ($z_H > 40$ m), this approach is justified and NEP can be calculated by:

$$NEP \left[gC\ m^{-2}\ (180\ days)^{-1} \right] = (AHM - RED) \times (106 / 138) \times (12 / 31) \times 180\ days \quad (7)$$

However, a high fraction of RED may already be oxidized in the oxic zone below the sediment-water interface and thus cause an enhanced SOU. Therefore, high allochthonous loads in deep lakes may contribute to increased SOU values and therefore, NEP would be overestimated by Equation 7. The proposed neglect of autochthonous OC deposits (ignoring NS) alleviates the potential NEP overestimation.

In lakes with $z_H < 40$ m, the contribution of autochthonous and allochthonous OC to O_2 consumption cannot be separated. Only a minor fraction of the settling OC from primary production is mineralized in the water column (Müller, Bryant, et al., 2012) but is deposited at the sediment surface where, O_2 provided, the main mineralization activity takes place. NS and the emerging RED consist of both, refractory OC from primary production and from allochthonous imports. As NS and RED cannot be clearly assigned to either of the two sources, NEP estimations would lead to large errors and the concept (Equation 7) is not applicable to lakes with $z_H < 40$ m that receive a substantial fraction of allochthonous OC.

Clear evidence for significant allochthonous inputs is difficult to find if it is not obvious from the characteristics of the lake, tributaries and the catchment. Indications can be obtained from a comparison of the C fraction in the sediment originating from NEP. In lakes where OC originates from autochthonous production, the percentage of NEP-C contained in the deposited sediment (NS-C) may serve as a lower limit. If the NS-C contribution is much higher than expected, based on experience from other lakes, then it is an indication that allochthonous OC may play a substantial role (details are provided in Section SI-2).

While import and export of nutrients is essential for the epilimnion budgeting methods (chapter 2.4), we neglect the import of OC into the water column of the hypolimnion during the stratified season. In lakes prone to occasional floodwaters, NEP may be overestimated due to enhanced O_2 depletion following high input of allochthonous OC into the hypolimnion.

In conclusion, we are able to estimate NEP for a wide range of lake types from only AHM, RED, and NS. Underestimations are unavoidable in some cases because it is challenging to determine NS accurately or to distinguish between autochthonous and allochthonous contributions in the sediment. A concise summary of arguments and decision support is given in Table SI-1. The line of thoughts is presented in the decision flow chart of Figure 3.

4. Results

4.1. Net Ecosystem Production in Deep Eutrophic Autochthonous Lakes (e.g., Lake Geneva)

Lake Geneva is one of the largest and deepest Western European lakes with a maximum depth and mean hypolimnion depth (z_H) of 309 and 151 m, respectively (Table 1). It has the highest AHM of all lakes considered, and one of the highest of this kind ($1.25 \pm 0.18\ gO_2\ m^{-2}\ d^{-1}$; 1966–2019; productive depth 15 m). The lake receives allochthonous material of low OC content from the mountainous and partly glaciated catchment (Loizeau & Dominik, 2000), but in its distant central basin, the areal OC deposition is limited (CIPEL, 1993). The input from the Rhône River is deposited mainly in the nearby delta (Randlett et al., 2015). The RED flux from the sediments of the main basin was almost negligible (3.6%, or $0.07\ gO_2\ m^{-2}\ d^{-1}$; Steinsberger, Schmid, et al., 2017). Therefore, we argue that AHM in Lake Geneva is almost entirely determined by settling autochthonous OC. Hence, NEP corresponds to the sum of AHM and NS (Figure 3; Table SI-1), and Equation 5 is applied resulting in $NEP = 70\ gC\ m^{-2}\ (180\ days)^{-1}$ (Table 2). The major fraction of OC (65

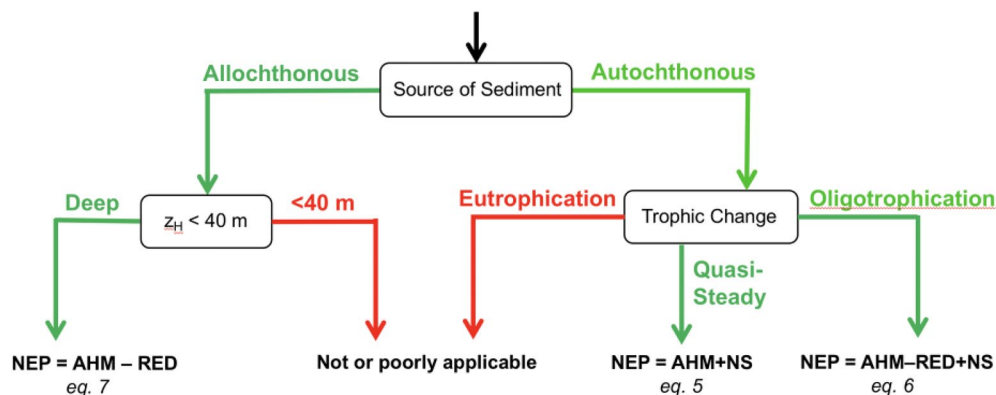


Figure 3. Decision flow chart depicting the procedure of NEP calculation according to individual lake characteristics.

$\text{gC m}^{-2} (180 \text{ days})^{-1}$ is mineralized within the oxic water body and sediment surface, corresponding to 92% of NEP (Figure 2, right hand side), leaving only $5 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ permanently buried in the sediment as NS (Table 2). Schwefel et al. (2018) have shown that of all hypolimnetic O_2 consumption, $\sim 70\%$ occurred in the water column (WCM) and only $\sim 30\%$ at the sediment surface (SOU).

A sediment trap study in 1978 by Lang and Hutter (1981) resulted in $79 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ which agrees well with our NEP estimate. While more recent sediment trap measurements exist for Lake Geneva, they had not been designed for NEP estimates, as they were exposed at depths too deep to suit for comparison, or were contaminated with allochthonous material (see discussion in Section SI-3).

4.2. Net Ecosystem Production in Eutrophic Autochthonous Lakes With $z_H < 40 \text{ m}$ (e.g., Lake Baldegg)

In the past 100 years, Lake Baldegg (Figure 1) with a maximum depth of 65 m and a mean hypolimnion depth of 25 m (Table 1) experienced a hypereutrophic phase with an anoxic hypolimnion that lasted until hypolimnetic aeration and forced winter mixing with compressed air was established in 1982 (Wehrli

Table 2
Summary of all Lake Data

Lake	AHM [$\text{gC m}^{-2} (180 \text{ days})^{-1}$]	RED [$\text{gC m}^{-2} (180 \text{ days})^{-1}$]	SOU [$\text{gC m}^{-2} (180 \text{ days})^{-1}$]	WCM [$\text{gC m}^{-2} (180 \text{ days})^{-1}$]	NS [$\text{gC m}^{-2} (180 \text{ days})^{-1}$]	NEP _{estim} [$\text{gC m}^{-2} (180 \text{ days})^{-1}$]	NEP _{trap} [$\text{gC m}^{-2} (180 \text{ days})^{-1}$]	Eq. for NEP _{estim} (–)
Maggiore	43.6	10.0	27.2	6.4	16.7	33.6	26.5 ¹	AHM – RED
Geneva	64.8	3.5	13.3	48.1	5.6	70.4		AHM + NS
Brienzen	28.0	2.3	13.1	12.6	18.4	25.7	9.8 ²	AHM – RED
Constance ^a	42.0	3.3	14.3	24.4	13.5	55.5	32.5 ³	AHM + NS
Thun	32.1	3.8	17.6	10.7	29.9	28.3		AHM – RED
Neuchâtel	35.8	5.1	17.6	13.0	12.0	30.7		AHM – RED
Lucerne ^b	18.1	1.0	18.3	~ 0	0.80	17.2	29.0 ⁴	AHM – RED
Walensee	31.1	6.0	29.2	~ 0	21.5	25.1		AHM – RED
Aegeri	31.1	6.9	19.2	4.9	11.4	24.2	12.2 ⁵	AHM – RED
Baldegg	65.8	25.4	38.5	1.9	22.8	63.2	42.5 ⁵	AHM – RED + NS
Hallwil	42.0	9.3	24.6	8.1	11.3	44.0	21.3 ⁵	AHM – RED + NS

Note. Oxygen depletion rates (AHM, RED, SOU, and WCM) were converted to mineralization rates of OC for the productive season (180 days) and expressed as [$\text{gC m}^{-2} (180 \text{ days})^{-1}$]. Correspondingly, NEP_{estim}, NS and NEP_{trap} are also given in [$\text{gC m}^{-2} (180 \text{ days})^{-1}$]. Sediment trap data (NEP_{trap}) is from ¹Callieri (1997), ²M. Sturm, pers. comm., ³Stabel (1986), ⁴Bloesch et al. (1977), and ⁵Steinsberger, Schmid, et al. (2017). No sediment trap data is available for Lakes Thun, Neuchâtel and Walensee. Sediment trap data for Lake Geneva were omitted for reasons discussed in the text and Section SI-3.

^aUpper Lake Constance. ^bVitznau Basin, a sub-basin of Lake Lucerne.

et al., 1997). Large amounts of only partly mineralized OC were buried in the sediment visible as a black, varved layer of ~30 cm thickness. Presently, the lake recovers towards mesotrophy and thanks to 40 years of artificial aeration, the sediment has turned from black to a light brown again indicating an intensified mineralization of the freshly settling OC (Steinsberger, Müller, et al., 2019). The remarkably high flux of RED from the sediment ($\sim 25 \text{ gC m}^{-2} (180 \text{ days})^{-1}$; Table 2; Steinsberger, Schmid, et al., 2017) is caused by the high production rate of CH_4 and NH_4^+ in the deposits from times of hypertrophy and anoxia. This “*sediment memory effect*” (Matzinger et al., 2010) consumes today $\sim 35\%$ of the AHM. A recent decrease in the deposition rate of OC in the Lake Baldegg sediments (NS) could not be established from sediment core analyses. However, this may be owed to the difficulty to accurately determine the sedimentation rate (mm yr^{-1}) in the recent deposits that would allow estimating NS.

In summary, for NEP estimation, the high RED was subtracted from AHM as it originates mainly from the past, but the fraction of OC buried in the sediments (NS) was included since we could not observe a significant decrease due to the expected oligotrophication as yet. Hence, Equation 6 was applied, which resulted in an NEP of $63 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ for Lake Baldegg. Sediment trap measurements yield a 33% lower estimate of $43 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ (Steinsberger, Schmid, et al., 2017). The discrepancy may partly be caused by overestimation of the current NEP and the notorious underestimation by sediment traps.

4.3. Net Ecosystem Production in Deep Oligotrophic Allochthonous Lakes (e.g., Lake Brienz)

Lake Brienz is a deep oligotrophic peri-alpine lake with a mountainous catchment. Primary production is very low with $\sim 50 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ (spring-summer average extracted from Figure 4b in Finger, Bossard, et al., 2007). Similar to Lake Geneva, NEP should be almost completely mineralized within the long water column and at the sediment surface (SOU). However, unlike Lake Geneva, Lake Brienz receives a high allochthonous particle load of $>300 \text{ kt yr}^{-1}$ (Finger, Schmid, & Wüest, 2006) due to its alpine catchment that is responsible for the high sedimentation rate of $1.2\text{--}2.3 \text{ cm yr}^{-1}$ in the deep lake basin (Anselmetti et al., 2007). The allochthonous sedimentation regime was well apparent also from sediment trap data. During the productive season of 2003, a sediment trap study measured $9.8 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ at 50 m depth, but $38 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ at 250 m depth (M. Sturm, pers. comm.), while Carstens et al. (2013) measured even more than twice of this amount ($89 \text{ gC m}^{-2} (180 \text{ days})^{-1}$) at 230 m water depth. The high NS ($18 \text{ gC m}^{-2} (180 \text{ days})^{-1}$) and RED ($2.3 \text{ gC m}^{-2} (180 \text{ days})^{-1}$) originate almost exclusively from allochthonous OC (Table 2). The low primary production and the comparatively large WCM ($13 \text{ gC m}^{-2} (180 \text{ days})^{-1}$) indicated that negligible NEP remained to be mineralized at or in the sediments. Due to the allochthonous dominance of OC inputs, we subtract RED from AHM and neglect NS as allochthonous, which results in NEP estimation according to Equation 7 of $26 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ (Table 2).

This value is higher than the result from the 50 m deep sediment trap mentioned above, most probably due to the too deep trap exposition. In support of the conclusions already drawn for sediment trap data from Lake Geneva, Carstens et al. (2013) reported for Lake Brienz that at 50 m depth, algae material exported from the productive zone was already largely degraded and partly replaced by bacterial OC growing on the slowing sinking particles. Deposition rates from bottom traps, however, exceeded the estimated NEP by far and were much higher than the ones measured at 50 m depth, thus illustrating convincingly that NS was dominated by allochthonous material and not related to NEP.

Therefore, not only RED but also almost all SOU (equivalent to $13 \text{ gC m}^{-2} (180 \text{ days})^{-1}$) must be caused by the mineralization of allochthonous OC (Table 2). Even though degradation rates of allochthonous OC are significantly lower than of autochthonous OC, Grasset et al. (2018) demonstrated that the accumulation of allochthonous OC over a long period can produce similar amounts of CH_4 as in autochthonous sediments. In lakes with very high loads of terrestrial material and low primary production, SOU can even exceed NEP (see Walensee and Lake Lucerne in Table 2).

SOU data from Lake Geneva represent an upper maximum, because this productive and deep lake is a role model for insignificant allochthonous inputs. The equivalent of $13 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ of Lake Geneva may therefore represent an upper limit for autochthonous SOU (Figure 4). Accordingly, higher SOU rates (up to ~ 2 times that of Lake Geneva, see Table 2) are not caused by the current NEP but must originate from the

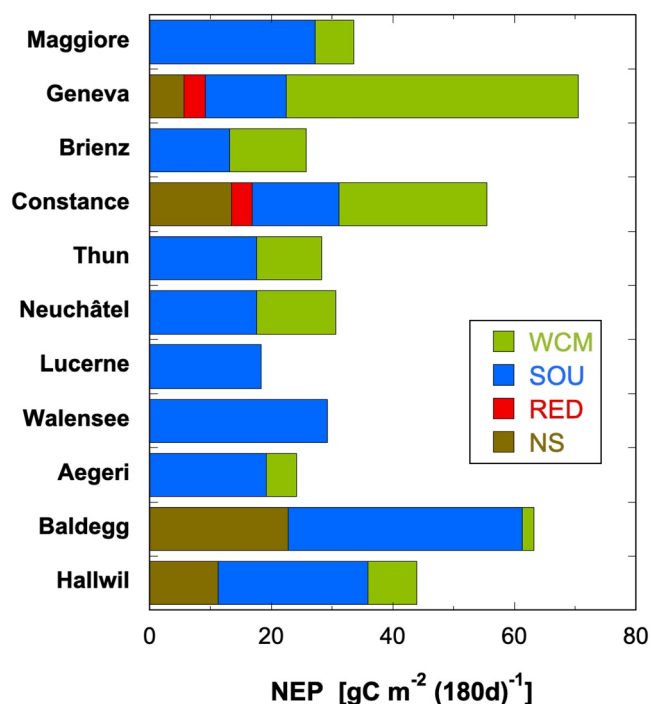


Figure 4. NEP estimations according to Equations 5, 6, or 7 for eleven lakes (ordered as in Tables 1 and 2) divided into the respective four domains of carbon sinks. RED is included in the NEP estimates only for Lakes Geneva and Constance (Table 2). Data from Steinsberger, Schwefel, et al. (2020).

in-sediment oxidation of RED. Consequently, in lakes with large allochthonous inputs, NEP may be overestimated.

5. Discussion

5.1. Challenges in the Estimation of Net Ecosystem Production

The export of OC from the productive surface zone of lakes to the hypolimnion can be estimated from routinely available monitoring data, net sedimentation, and the flux of reduced substances from the sediment. This simple concept can readily be applied when lakes are in quasi-steady conditions with respect to their trophic level, and production is mainly autochthonous. In this case, NEP is simply the sum of O_2 depletion and the accumulation of OC in the sediment. If a lake is in transition from eutrophic to oligotrophic or vice versa, the challenge is to estimate the representative NS, which is obviously varying over time. Moreover, RED does not correspond to the present NEP but is generated by the deposition caused by former lake productivity. A second challenge is the import of terrestrial OC from their catchment that increases NS and RED, and can consume additional O_2 . These two aspects are discussed below. The decision flow chart (Figure 3) is designed to help finding the optimal approach for NEP estimation.

1. **The ideal case**—The concept proved well applicable for deep lakes that received only small amounts of allochthonous inputs of OC, such as Lakes Geneva and Constance. Mineralization of the autochthonous OC in deep lakes is accomplished in the oxic water column (WCM) and at the sediment surface (SOU) (Figure 2). Only small fractions of OC remained buried as NS or caused RED fluxes. Lake Geneva fulfills both requirements of (1) a long-term steady-state trophic level and of (2) small allochthonous loads. At present, there are no indications that productivity decreased significantly, and at sufficient distance from the Rhône River inflow, deposition of OC may be entirely autochthonous. Therefore, we considered NEP to be composed of AHM plus NS and Equation 5 to be adequate. Lake Constance is mesotrophic today and recovering from the past eutrophic phase with TP concentrations of up to $\sim 90 \text{ mg m}^{-3}$ at the end of the 1970's. Total P concentrations after winter overturn are $< 10 \text{ mg m}^{-3}$ since 2006 and therefore we assume that sediment processes are also at steady-state with the current production and calculate NEP as the sum of AHM plus NS, identical to Lake Geneva.
2. **Allochthonous perturbations**—Similar to Lakes Geneva and Constance, a large fraction of NEP in the deep Lakes Maggiore, Brienz, Thun, Neuchâtel, Lucerne, and Walensee was also mineralized in the water column (WCM) (For Lake Aegeri, see the comment in Section SI-4). However, even though these lakes are clearly oligo- to mesotrophic with TP_{mix} concentrations $< 12 \text{ mg m}^{-3}$ (Table 1), the fraction of OC mineralized at the sediment surface (SOU, Figure 4) was considerably higher than for Lakes Geneva and Constance. The lakes are not much shallower but receive an increased share of more refractory OC due to their large and steep peri-alpine catchments (Table 2). In the oligotrophic Lakes Lucerne and Walensee, the measured SOU was so high that the difference between AHM and SOU, which is the mineralization in the water column (WCM), was smaller than the uncertainty of these rates (Figure 2). The fraction of the allochthonous contribution cannot be quantified. However, as Lakes Geneva and Constance represent end members of lakes with minimal input of allochthonous OC and extensive mineralization of the autochthonous production in the water column, their SOU values provide a lowermost bound for the mineralization of autochthonous OC.

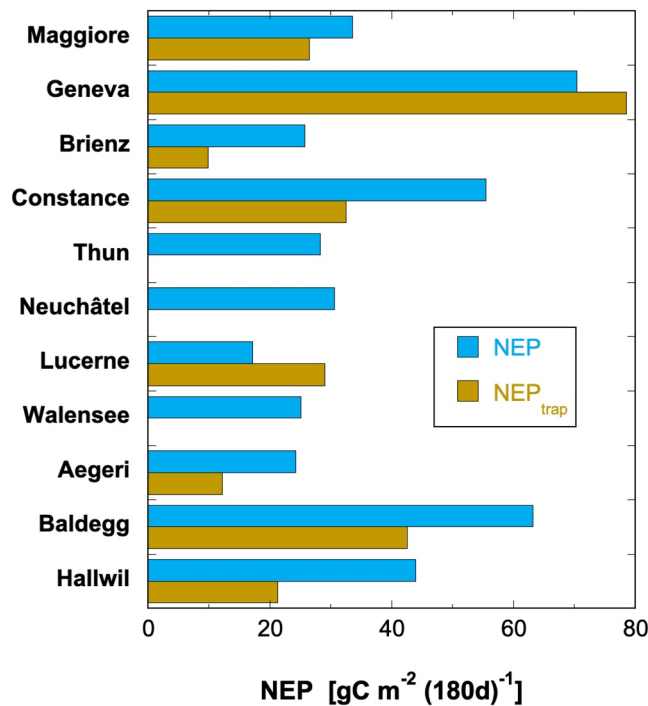


Figure 5. Comparison between NEP estimations from O₂ depletion (blue) and NEP from trap measurements (NEP_{trap}, brown). Note that most of the NEP_{trap} values were taken from the literature and were not measured at the same time and/or location as the values for NEP. For Lakes Neuchâtel, Thun, and Walensee no sediment trap data are available.

3. **Nonsteady-state level of trophic**—Lakes Baldegg and Hallwil are productive lakes with $z_H < 40$ m and no detectable allochthonous inputs but still suffering from their eutrophic past. Their high sediment OC content and, accordingly, high flux of CH₄ and NH₄⁺ from the sediment (RED) originate largely from these past periods and do not reflect the present NEP. Therefore, we consider these lakes not at steady-state and in accordance with Equation 6, RED is subtracted for the estimation of the current NEP. Today, a large fraction of the settling autochthonous OC is mineralized in the water column or at the sediment surface. As it is not possible to determine the contemporary OC sedimentation rate, the NEP will be slightly underestimated when RED is neglected and Equation 6 is applied.

5.2. Comparison of Net Ecosystem Production Estimations With Sediment Trap Measurements

Direct measurements of NEP can be performed with sediment trap measurements. Operating sediment traps in the field is extremely laborious and time consuming, and accordingly, relatively few full data sets are available. Sediment trap results (NEP_{trap}) from at least one full year for each lake are collected from the literature and presented in Figure 5 (brown bars) and compared with estimated NEP values from this work (blue bars). We observed a moderate agreement between our estimated NEP and sediment trap measurements that may be partly explained by the limited duration of sediment trap expositions, too deep exposure depth (e.g., Lake Brienz; Carstens et al., 2013), annual variability, method-inherent difficulties of quantitative sampling and the underestimation of accumulation because of mineralization of OC during trap exposition.

5.3. Estimation of NEP From Epilimnetic Mass Balances of P and N

Phosphorus and nitrogen are essential elements for primary production and are thus assimilated in distinct ratios (Redfield et al., 1963). Therefore, the removal of P and N from the productive surface layer of lakes corresponds to the export rate of organic matter. The areal removal rate can be calculated provided that the uptake ratio (C:N:P) is known. While the Redfield ratio C:N:P of 106:16:1 is rather the exception than the rule, even in oceans, this ratio is clearly higher and much more variable in freshwater lakes (Hecky et al., 1993; Hessen, 2006; Moreno & Martiny, 2018; Sterner et al., 2008). In fact, the annual average C:P ratio of freshwater lake seston captured by sediment traps was found to increase with progressing oligotrophication from ~80 to >250 (Müller, Steinsberger, Schwefel, et al., 2019). Therefore, if the C:P:N ratio of the particulate OC exported from the productive zone can be determined representatively, an alternative way of estimating NEP from epilimnion budgets of P and N would be available. Such high quality nutrient data, including adequate temporal resolution of the C:P:N ratios of the seston, were only available for Lake Geneva.

Epilimnion budgets for P and N over the stratified season require measurements of loads, export, and changes of the water column content between the onset and the end of the stratified season (Equations 2 and 3). We used the lake volume of the top 30 m for the epilimnion budget because the nutrient depletion was apparent to at least 30 m depth, which is also considered the lowermost depth of primary production (Anneville et al., 2019; Fernández-Castro et al., 2021). Total dissolved P and nitrate (NO₃⁻) loads from tributaries were considered as bio-available species. A complete data set over 48 years of water column measurements, including analyses of particulate OC, P and N, and loads of dissolved P and N from tributaries to Lake Geneva, resulted in NEP estimates presented in Figure 6.

The long-term averages of NEP estimations from AMH (red in Figure 6: 70 ± 9 gC m⁻² (180 days)⁻¹) and epilimnion budgets of P (blue: 52 ± 13 gC m⁻² (180 days)⁻¹) and N (green: 50 ± 14 gC m⁻² (180 days)⁻¹)

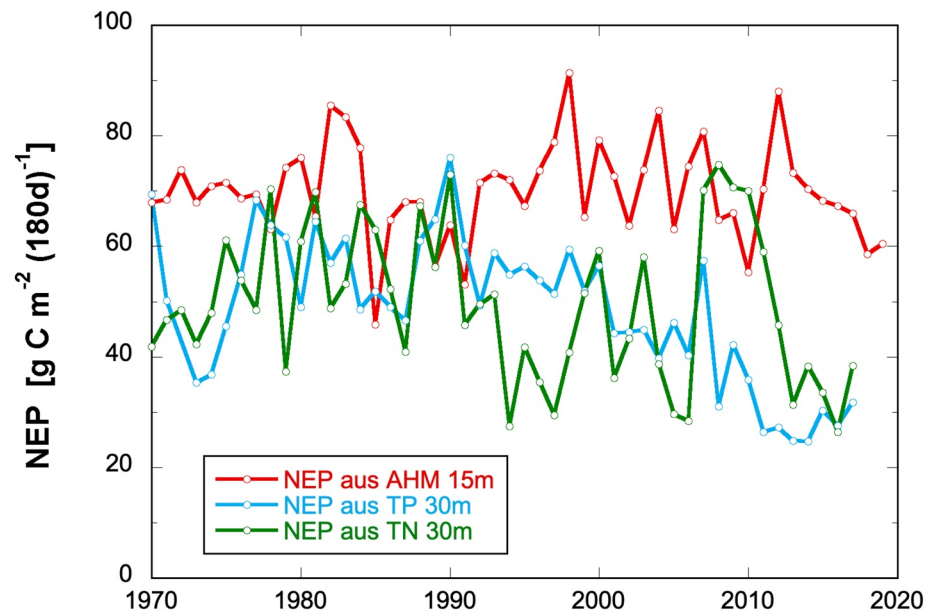


Figure 6. Net ecosystem production (NEP, in $\text{gC m}^{-2} (180 \text{ days})^{-1}$) of Lake Geneva estimated from the hypolimnetic O_2 consumption rate, AHM (red, $70 \pm 9 \text{ gC m}^{-2} (180 \text{ days})^{-1}$), according to Equation 5; estimated from the epilimnion balance of P (blue, $52 \pm 13 \text{ gC m}^{-2} (180 \text{ days})^{-1}$; Equation 2) and N (green, $50 \pm 14 \text{ gC m}^{-2} (180 \text{ days})^{-1}$; Equation 3). Calculations cover the stratified productive season of 180 days (April to October). Productive surface layer depth for P and N budgets was 30 m.

agree reasonably well considering the very different approaches. For such a large sized lake the amount of data (biweekly profiles at one single sampling location) used for upscaling to the whole system is small compared with the dimensions of the water body. This is advantageous for the simplicity of the method presented but leads to large fluctuations. Metabolic rates determined by Fernández-Castro et al. (2021) with high-frequency measurements of dissolved O_2 during the stratified season of 2019 resulted in NEP estimates of $73\text{--}110 \text{ gC m}^{-2}$ for the top 8.75 m, and 50 to $89 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ for the top 30 m. Our estimated NEP assuming 15 m productive depth of $70 \pm 9 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ fits well in between these ranges.

Temporal scatter seems reasonable in view of the substantial errors involved in the epilimnetic P and N budgets (Equations 2 and 3). Another source of error is that later in the season, C:P ratios can drastically increase on short terms, as P concentrations approach detection limits, and therefore a temporally highly resolved sampling would be required for an accurate budget. No systematic trend was apparent except for a decrease of NEP estimated from the P balance in recent years, which may indicate that O_2 depletion potentially responds with some delay to reoligotrophication. With a sufficient number of O_2 measurements, AHM is more accurate than the nutrient budget and we therefore consider the nutrient budget more as a plausibility check for detection of discrepancies.

5.4. Export Ratio

Comparison of the NEP estimates with primary production rates results in the “*export ratio*” (Reynolds, 1984) for Lake Geneva. The export ratio is the ratio of the sinking flux of OC from the trophic zone (here NEP) in $\text{gC m}^{-2} (180 \text{ days})^{-1}$ and the depth-integrated primary production ($\text{gC m}^{-2} \text{ d}^{-1}$) (Baines & Pace, 1994). Using the value of $208 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ estimated from the CIPEL primary production measurements (C. Minaudo, pers. comm.) for the productive period (April to September) of the years 2015–2019, and the NEP of $70 \text{ gC m}^{-2} (180 \text{ days})^{-1}$ estimated in this work results in an export ratio of 34%. This signifies that two thirds of the OC assimilated in Lake Geneva was mineralized again within the productive zone. Baines and Pace (1994) found that export rates of 30%–50% were characteristic for oligotrophic lakes, while in eutrophic lakes export rates decreased to 10%–30% as production increased. This indicates that Lake Geneva is

in a trophic transition moving from eutrophic to mesotrophic, suggesting that the observed export ratio of one third is consistent with values reported in the literature.

6. Conclusions

In summary, as the O_2 depletion is directly coupled to the settling OC and as the O_2 depletion is the key important information for water quality management, we consider the proposed NEP estimation approach as robust and informative. In principle, the presented hypolimnion budget approach should be applicable to all seasonally stratified lakes. The application needs critical pre-evaluation for lakes with an average hypolimnion depth <40 m dominated by allochthonous inputs of OC, and for lakes undergoing eutrophication. The challenge is to proof that the conditions for the application of the approach are fulfilled, which may not be well defined in each individual case. Table SI-1 and Figure 3 provide important guidance, and the use of the epilimnion nutrient budget support the identification of inconsistencies. Although we acknowledge that this approach has substantial errors, we consider the results as robust as they are based on primary field data and allow recognizing accurate temporal trends. Great advantages are (1) the simple data acquisition and analysis based on often-available routine monitoring, (2) the robustness of the estimates due to season-long time-integration, and (3) the applicability to historic data and subsequent temporal trend evaluation.

Data Availability Statement

All data and information relevant to this article are available at <https://doi.org/10.25678/0003M5>.

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References

- Anneville, O., Chang, C. W., Dur, G., Souissi, S., Rimet, F., & Hsieh, C. H. (2019). The paradox of re-oligotrophication: The role of bottom-up versus top-down controls on the phytoplankton community. *Oikos*, 128(11), 1666–1677. <https://doi.org/10.1111/oik.06399>
- Anselmetti, F. S., Bühler, R., Finger, D., Girardclos, S., Lancini, A., Rellstab, C., & Sturm, M. (2007). Effects of Alpine hydropower dams on particle transport and lacustrine sedimentation. *Aquatic Sciences*, 69(2), 179–198. <https://doi.org/10.1007/s00027-007-0875-4>
- Baines, S. B., & Pace, M. L. (1994). Relationships between suspended particulate matter and sinking flux along a trophic gradient and implications for the fate of planktonic primary production. *Canadian Journal of Fisheries and Aquatic Sciences*, 51(1), 25–36. <https://doi.org/10.1139/f94-005>
- Bloesch, J., Stadelmann, P., & Bühler, H. (1977). Primary production, mineralization, and sedimentation in the euphotic zone of two Swiss lakes. *Limnology and Oceanography*, 22(3), 511–526. <https://doi.org/10.4319/lo.1977.22.3.0511>
- Briggs, N., Guðmundsson, K., Cetinić, I., D'Asaro, E., Rehm, E., Lee, C., & Perry, M. J. (2018). A multi-method autonomous assessment of primary productivity and export efficiency in the springtime North Atlantic. *Biogeosciences*, 15(14), 4515–4532. <https://doi.org/10.5194/bg-15-4515-2018>
- Callieri, C. (1997). Sedimentation and aggregate dynamics in Lake Maggiore, a large, deep lake in Northern Italy. *Memorie-Istituto Italiano di Idrobiologia*, 56, 37–50.
- Cannata, M., Lepori, F., & Capelli, C. (2020). *SoftLake (version beta-0.1)*. Zenodo. <https://doi.org/10.5281/zenodo.3618219>
- Carey, C. C., Doubek, J. P., McClure, R. P., & Hanson, P. C. (2018). Oxygen dynamics control the burial of organic carbon in a eutrophic reservoir. *Limnology and Oceanography*, 3(3), 293–301. <https://doi.org/10.1002/lol2.10057>
- Carstens, D., Lehmann, M. F., Hofstetter, T. B., & Schubert, C. J. (2013). Amino acid nitrogen isotopic composition patterns in lacustrine sedimenting matter. *Geochimica et Cosmochimica Acta*, 121, 328–338. <https://doi.org/10.1016/j.gca.2013.07.020>
- Charlton, M. N. (1980). Hypolimnion oxygen consumption in lakes: discussion of productivity and morphometry effects. *Canadian Journal of Fisheries and Aquatic Sciences*, 37(10), 1531–1539. <https://doi.org/10.1139/f80-198>
- CIPEL. (1993). *Annual scientific reports of the Commission Internationale pour la Protection des Eaux du Léman (CIPEL)*. Retrieved from <https://www.cipel.org/publications/rapports-scientifiques/>
- CIPEL. (2020). *Annual scientific reports of the Commission Internationale pour la Protection des Eaux du Léman (CIPEL)*. Retrieved from <https://www.cipel.org/publications/rapports-scientifiques/>
- DEV. (2002). *German standard methods for the examination of water, wastewater and sludge*. Wiley-VCH. ISBN 978-3-410-13028-4. Since 1960.
- Epping, E. H. G., & Helder, W. (1997). Oxygen budgets calculated from in situ oxygen microprofiles for Northern Adriatic sediments. *Continental Shelf Research*, 17(14), 1737–1764. [https://doi.org/10.1016/S0278-4343\(97\)00039-3](https://doi.org/10.1016/S0278-4343(97)00039-3)
- Fernández-Castro, B., Chmiel, H. E., Minaudo, C., Krishna, S., Perolo, P., Rasconi, S., & Wüest, A. (2021). Primary and net ecosystem production in a large lake diagnosed from high-resolution oxygen measurements. *Water Resources Research*, e2020WR029283. <https://doi.org/10.1029/2020wr029283>
- Finger, D., Bossard, P., Schmid, M., Jaun, L., Müller, B., Steiner, D., et al. (2007). Effects of alpine hydropower operations on primary production in a downstream lake. *Aquatic Sciences*, 69(2), 240–256. <https://doi.org/10.1007/s00027-007-0873-6>
- Finger, D., Schmid, M., & Wüest, A. (2006). Effects of upstream hydropower operation on riverine particle transport and turbidity in downstream lakes. *Water Resources Research*, 42(8), W08429. <https://doi.org/10.1029/2005WR004751>
- Franchini, F., Lepori, F., & Bruder, A. (2017). Improving estimates of primary production in lakes: a test and a case study from a peri-alpine lake (Lake Lugano). *Inland Waters*, 7(1), 77–87. <https://doi.org/10.1080/20442041.2017.1294351>

- Giling, D. P., Staehr, P. A., Grossart, H. P., Andersen, M. R., Boehrer, B., Escot, C., et al. (2017). Delving deeper: Metabolic processes in the metalimnion of stratified lakes. *Limnology and Oceanography*, 62(3), 1288–1306. <https://doi.org/10.1002/lno.10504>
- Grasset, C., Mendonça, R., Villamor Saucedo, G., Bastviken, D., Roland, F., & Sobek, S. (2018). Large but variable methane production in anoxic freshwater sediment upon addition of allochthonous and autochthonous organic matter. *Limnology and Oceanography*, 63(4), 1488–1501. <https://doi.org/10.1002/lno.10786>
- GSM. (2002). *German standard methods for the examination of water, wastewater and sludge*. Wiley VCH. (in German).
- Hargrave, B. T. (1972). A comparison of sediment oxygen uptake, hypolimnetic oxygen deficit and primary production in Lake Esrom, Denmark. *Internationale Vereinigung für theoretische und angewandte Limnologie: Verhandlungen*, 18(1), 134–139. <https://doi.org/10.1080/036800770.1971.11895975>
- Hecky, R. E., Campbell, P., & Hendzel, L. L. (1993). The stoichiometry of carbon, nitrogen, and phosphorus in particulate matter of lakes and oceans. *Limnology and Oceanography*, 38(4), 709–724. <https://doi.org/10.4319/lno.1993.38.4.0709>
- Hessen, D. O. (2006). Determinants of seston C: P-ratio in lakes. *Freshwater Biology*, 51(8), 1560–1569. <https://doi.org/10.1111/j.1365-2427.2006.01594.x>
- Lang, C., & Hutter, P. (1981). Structure, diversity and stability of two oligochaete communities according to sedimentary inputs in Lake Geneva (Switzerland). *Schweizerische Zeitschrift für Hydrologie*, 43(2), 265–276. <https://doi.org/10.1007/bf02502137>
- Li, J., Crowe, S. A., Miklesh, D., Kistner, M., Canfield, D. E., & Katsev, S. (2012). Carbon mineralization and oxygen dynamics in sediments with deep oxygen penetration, Lake Superior. *Limnology and Oceanography*, 57(6), 1634–1650. <https://doi.org/10.4319/lno.2012.57.6.1634>
- Li, Y.-H., & Gregory, S. (1974). Diffusion of ions in sea water and in deep-sea sediments. *Geochimica et Cosmochimica Acta*, 38(5), 703–714. [https://doi.org/10.1016/0016-7037\(74\)90145-8](https://doi.org/10.1016/0016-7037(74)90145-8)
- Loizeau, J.-L., & Dominik, J. (2000). Evolution of the Upper Rhone River discharge and suspended sediment load during the last 80 years and some implications for Lake Geneva. *Aquatic Sciences*, 62(1), 54–67. <https://doi.org/10.1007/s000270050075>
- Maerki, M., Müller, B., Dinkel, C., & Wehrli, B. (2009). Mineralization pathways in lake sediments with different oxygen and organic carbon supply. *Limnology and Oceanography*, 54(2), 428–438. <https://doi.org/10.4319/lno.2009.54.2.0428>
- Maerki, M., Müller, B., & Wehrli, B. (2006). Microscale mineralization pathways in surface sediments: A chemical sensor study in Lake Baikal. *Limnology and Oceanography*, 51(3), 1342–1354. <https://doi.org/10.4319/lno.2006.51.3.1342>
- Maerki, M., Wehrli, B., Dinkel, C., & Müller, B. (2004). The influence of tortuosity on molecular diffusion in freshwater sediments of high porosity. *Geochimica et Cosmochimica Acta*, 68(7), 1519–1528. <https://doi.org/10.1016/j.gca.2003.09.019>
- Marcé, R., George, G., Buscarin, P., Deidda, M., Dunalska, J., De Eyto, E., et al. (2016). Automatic high frequency monitoring for improved lake and reservoir management. *Environmental Science & Technology*, 50(20), 10780–10794. <https://doi.org/10.1021/acs.est.6b01604>
- Matzinger, A., Müller, B., Niederhauser, P., Schmid, M., & Wüest, A. (2010). Hypolimnetic oxygen consumption by sediment-based reduced substances in former eutrophic lakes. *Limnology and Oceanography*, 55(5), 2073–2084. <https://doi.org/10.4319/lno.2010.55.5.2073>
- Moreno, A. R., & Martiny, A. C. (2018). Ecological stoichiometry of ocean plankton. *Annual Review of Marine Science*, 10, 43–69. <https://doi.org/10.1146/annurev-marine-121916-063126>
- Müller, B., Bryant, L. D., Matzinger, A., & Wüest, A. (2012). Hypolimnetic oxygen depletion in eutrophic lakes. *Environmental Science & Technology*, 46(18), 9964–9971. <https://doi.org/10.1021/es301422r>
- Müller, B., Steinsberger, T., Schwefel, R., Gächter, R., Sturm, M., & Wüest, A. (2019). Oxygen consumption in seasonally stratified lakes decreases only below a marginal phosphorus threshold. *Scientific Reports*, 9(1), 18054. <https://doi.org/10.1038/s41598-019-54486-3>
- Müller, B., Steinsberger, T., & Wüest, A. (2021). Increasing carbon-to-phosphorus ratio (C:P) from seston as a prime indicator for the initiation of lake reoligotrophication. *Environmental Science & Technology*. (in print). <https://doi.org/10.1021/acs.est.0c08526>
- Müller, B., Wang, Y., Dittrich, M., & Wehrli, B. (2003). Influence of organic carbon decomposition on calcite dissolution in surficial sediments of a freshwater lake. *Water Research*, 37(18), 4524–4532. [https://doi.org/10.1016/S0043-1354\(03\)00381-6](https://doi.org/10.1016/S0043-1354(03)00381-6)
- Obrador, B., Staehr, P. A., & Christensen, J. P. C. (2014). Vertical patterns of metabolism in three contrasting stratified lakes. *Limnology and Oceanography*, 59(4), 1228–1240. <https://doi.org/10.4319/lno.2014.59.4.1228>
- Och, L. M., Müller, B., Voegelin, A., Ulrich, A., Göttlicher, J., Steiniger, R., et al. (2012). New insights into the formation and burial of Fe/Mn accumulations in Lake Baikal sediments. *Chemical Geology*, 330–331, 244–259. <https://doi.org/10.1016/j.chemgeo.2012.09.011>
- Råman Vinnå, L., Medhaug, I., Schmid, M., & Bouffard, D. (2021). The vulnerability of lakes to climate change along an altitudinal gradient. *Communications Earth & Environment*, 2, 35. <https://doi.org/10.1038/s43247-021-00106-w>
- Randlett, M.-E., Sollberger, S., Del Sontro, T., Müller, B., Corella, J. P., Wehrli, B., & Schubert, C. J. (2015). Mineralization pathways of organic matter deposited in a river-lake transition of the Rhone River Delta, Lake Geneva. *Environmental Sciences: Processes & Impacts*, 17(2), 370–380. <https://doi.org/10.1039/c4em00470a>
- Redfield, A. C., Ketchum, B. H., Richards, F. A., The Sea, & Hill, M. N. (1963). The influence of organisms on the composition of sea-water. In M. N. Hill (Ed.), *The Sea* (pp. 26–77).
- Reynolds, C. S. (1984). *The ecology of the freshwater phytoplankton*. Cambridge University Press.
- Rimet, F., Anneville, O., Barbet, D., Chardon, C., Crépin, L., Domaizon, I., et al. (2020). The Observatory on LAKes (OLA) database: Sixty years of environmental data accessible to the public. *Journal of Limnology*, 79(2), 164–178. <https://doi.org/10.4081/jlimnol.2020.1944>
- Schwefel, R., Steinsberger, T., Bouffard, D., Bryant, L. D., Müller, B., & Wüest, A. (2018). Using small-scale measurements to estimate hypolimnetic oxygen depletion in a deep lake. *Limnology and Oceanography*, 63(S1), S54–S67. <https://doi.org/10.1002/lno.10723>
- Stabel, H.-H. (1986). The role of plankton biomass in controlling fluctuations of suspended matter in Lake Constance. *Hydrobiologia*, 140(2), 173–181. <https://doi.org/10.1007/bf00007572>
- Staehr, P. A., Christensen, J. P. A., Batt, R. D., & Read, J. S. (2012). Ecosystem metabolism in a stratified lake. *Limnology and Oceanography*, 57(5), 1317–1330. <https://doi.org/10.4319/lno.2012.57.5.1317>
- Steinsberger, T., Müller, B., Gerber, C., Shafel, B., & Schmid, M. (2019). Modeling sediment oxygen demand in a highly productive lake under various trophic scenarios. *PloS One*, 14(10), e0222318. <https://doi.org/10.1371/journal.pone.0222318>
- Steinsberger, T., Schmid, M., Wüest, A., Schwefel, R., Wehrli, B., & Müller, B. (2017). Organic carbon mass accumulation rate regulates the flux of reduced substances from the sediments of deep lakes. *Biogeosciences*, 14(13), 3275–3285. <https://doi.org/10.5194/bg-14-3275-2017>
- Steinsberger, T., Schwefel, R., Wüest, A., & Müller, B. (2020). Hypolimnetic oxygen depletion rates in deep lakes: Effects of trophic state and organic matter accumulation. *Limnology and Oceanography*, 65(12), 3128–3138. <https://doi.org/10.1002/lno.11578>
- Sterner, R. W., Andersen, T., Elser, J. J., Hessen, D. O., Hood, J. M., McCauley, E., & Urabe, J. (2008). Scale-dependent carbon:nitrogen:phosphorus seston stoichiometry in marine and freshwaters. *Limnology and Oceanography*, 53(3), 1169–1180. <https://doi.org/10.4319/lno.2008.53.3.1169>
- Stumm, W., & Morgan, J. J. (1996). *Aquatic chemistry* (3rd ed.). Wiley.

- Torres, N. T., Hauser, P. C., Furrer, G., Brandl, H., & Müller, B. (2013). Sediment porewater extraction and analysis combining filter tube samplers and capillary electrophoresis. *Environmental Sciences: Processes & Impacts*, 15(4), 715–720. <https://doi.org/10.1039/c3em00068k>
- Torres, N. T., Och, L. M., Hauser, P. C., Furrer, G., Brandl, H., Vologina, E., et al. (2014). Early diagenetic processes generate iron and manganese oxide layers in the sediments of Lake Baikal, Siberia. *Environmental Sciences: Processes & Impacts*, 16(4), 879–889. <https://doi.org/10.1039/c3em00676j>
- Wehrli, B., Lotter, A. F., Schaller, T., & Sturm, M. (1997). High-resolution varve studies in Baldeggersee (Switzerland): Project overview and limnological background data. *Aquatic Sciences*, 59(4), 285–294. <https://doi.org/10.1007/s000270050015>
- Wetzel, R. G. (2001). *Limnology* (3rd ed.). Academic Press.