Mineralization of autochthonous particulate organic carbon is a fast channel of organic matter turnover in Germany's largest drinking water reservoir

Marlene Dordoni [1], Michael Seewald [2], Karsten Rinke [2], Kurt Friese[2], Robert van Geldern [1], Jakob Schmidmeier [1], Johannes A.C. Barth [1]

[1] Friedrich- Alexander-Universität Erlangen-Nürnberg (FAU), Department of Geography and Geosciences, GeoZentrum Nordbayern, Schlossgarten 5, Erlangen, 91054, Germany
[2] Helmholtz Centre for Environmental Research-UFZ, Brueckstrasse 3a, D-39114, Magdeburg, Germany

Correspondence to: Marlene Dordoni (marlene.dordoni@fau.de)

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Abstract. Turnover of organic matter (OM) is an essential ecological function in inland water bodies and relevant for water quality. This is especially important for the potential of dissolved organic carbon (DOC) removal as well as ~~due~~ for~~to~~ emissions of CO_2. In this study, ~~We~~ we investigated various ~~sources~~ phases of OM including DOC, autochthonous particulate organic carbon (auto-POC), allochthonous particulate organic carbon (allo-~~Ext~~POC), and sedimentary matter (SED) in a temperate drinking water reservoir (Rappbode Reservoir, Germany) ~~with respect to~~by means of dissolved inorganic carbon (DIC) concentrations and carbon stable isotope ratios of DIC and OM. ~~and concentration dynamics~~. ~~For this purpose, w~~In order to best outline the turnover ~~W~~we focused on the metalimnion and the hypolimnion of the reservoir, where respiratory turnover is expected to be dominant and hardly disturbed by atmospheric exchange or photosynthesis. ~~The observation period of nine months covered a complete stratification period of the water body. Dissolved inorganic carbon (DIC) concentrations and its isotopes ($\delta^{13}C_{DIC}$) were considered together with isotope data of DOC and POC ($\delta^{13}C_{DOC}$ and $\delta^{13}C_{POC}$) as input parameters for mass balances.~~ DIC concentrations ranged between 0.30 and 0.53 mmol L^{-1}, while $\delta^{13}C_{DIC}$ values ~~were~~ ranged between -15.1 and -7.2 ‰ versus the VPDB (Vienna PeeDee Belemnite) standard. Values of $\delta^{13}C_{DOC}$ and $\delta^{13}C_{\text{auto-}}$~~$_{P}$~~$_{POC}$ ranged between -28.8 and -27.6 ‰ and between -35.2 and -26.8 ‰, respectively. Isotope compositions of sedimentary material and allochthonous POC were inferred from the literature~~bibliographic sources relevant for the study site~~ and from measurements from previous with ~~average~~ values of $\delta^{13}C_{SED}$ = -31~~0~~.~~7~~1 ‰, and $\delta^{13}C_{\text{allo-}}$~~$_{Ext}$~~$_{POC}$ ranging from ~~=~~ -31.8 ‰ and -28.6 ‰. Comparison of DIC concentration gains and stable isotope mass balances showed that autochthonous POC from primary producers was the main contributor to ~~DIC~~ increases of the DIC pool~~, while contributions from DOC, ExtPOC and SED played a minor role~~. Based on confirmed DIC gains by isotope mass balances calculated OM turnover rates~~, i.e. the conversion of organic carbon towards DIC, calculated with our isotope approach~~ were within the range for oligotrophic water bodies (0.01 to 1.3 µmol L^{-1} d^{-1}). Some higher values in the metalimnion are likely due to increased ~~the~~ availability of settling auto-POC from the photic zone. Samples from a Metalimnetic Oxygen Minimum (MOM) showed also showed ~~a clear~~ dominance of respiration over photosynthesis~~ through bacterial degradation of auto-chthonous POC~~. These high turnover rates ~~further highlight a close link with~~are likely related to planktonic biological assemblages. Our work shows that respiration in temperate lentic water bodies largely depends on auto-~~chthonous~~ POC production as a major carbon source. Such dependencies can influence vulnerabilities of these aqueous systems~~.~~

1~~.~~ Introduction

Among the carbon phases in terrestrial surface waters, dissolved inorganic carbon (DIC) is usually most abundant, with concentrations that range from 0.1 mmol L^{-1} to more than 1.0 mmol L^{-1} ~~in lentic water bodies~~ (Cole and Praire, 2014). This wide range of concentrations ~~is~~ also ~~closely~~ linksed to metabolic processes, because DIC is at the same time a reagent for photosynthesis and a product of respiration. Respiration rates vary with temperature, organic matter load and nutrient availability and phytoplankton assemblages (Gattuso et al., 2002; Hanson et al., 2003; Pace and Prairie, 2005; Wu and Chen, 2011; Mazuecos et al., 2015). A fundamental contribution to DIC budgets in water systems is represented by atmospheric and soil CO_2. For instance, ~~A~~atmospheric CO_2 influences DIC concentrations through the entire water column of lentic bodies during the mixing period, while it mainly affects the epilimnion during stratification periods. Because of its high solubility in waters, this gas plays a major role in the shallower parts of lentic aquatic ecosystems from which it either degasses (in case of heterotrophy) or it ~~gets~~becomes dissolved from the atmosphere (autotrophy) into the surface layer (Wetzel, 1984; Cole et al., 2007; Tranvik et al., 2009; Raymond et al., 2013; Koschorreck et al., 2017; DelSontro et al., 2018). On the other hand, carbon contributions from OM to the DIC pools ~~are~~ usually become important at ~~deeper levels~~greater water depths. ~~This~~Such respiratory turnover is particularly important~~true~~ for the hypolimnion of eutrophic lakes and reservoirs, where a substantial increase in total inorganic carbon (ΣCO_2) ~~is~~can often be observed ~~due to the combination of various decompositional processes~~ (Wetzel, 1983). This feature is far less marked in oligotrophic lentic water bodies. ~~Because of its high solubility in waters, this gas plays a major role in the shallower parts of lentic aquatic ecosystems from which it either degasses (in case of heterotrophy) or it gets dissolved from the atmosphere (autotrophy) into the surface layer (Wetzel, 1984; Cole et al., 2007; Tranvik et al., 2009; Raymond et al., 2013; Koschorreck et al., 2017; DelSontro et al., 2018).~~

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Other carbon phases in waters are represented by organic matter (OM). Organic carbon compounds result from decomposition processes of dead organic matter within (i.e. autochthonous) or outside (i.e. allochthonous) a water body (Kritzberg et al., 2004). Almost all authochnous material in the pelagic zone of a water body consists of ~~dissolved organic carbon (DOC) and~~ dead particulate organic carbon (auto-POC) and, to a smaller extent, dissolved organic carbon generated by leaching (Wetzel, 1984). Only a small fraction accounts for living biota (Kawasaki and Benner, 2006). Allochthonous OM is primarily of terrestrial plant origin and is transported to lentic systems by runoff as dissolved or particulate phase (~~Ext~~allo-DOC and allo-~~Ext~~POC). To a minor extent ~~A~~allo-~~Ext~~DOC and allo-~~Ext~~POC phases can also derive from atmospheric inputs such as transport of dust by wind (Willey et al., 2000). ~~In most cases, ExtDOC and ExtPOC concentrations are subject to seasonal variations.~~ Residual autochthonous and allochthonous carbon that reach the bottom of a lentic water body can accumulate and generate sedimentary organic carbon (SED). This carbon burial in sediments is one of the main mechanisms of carbon sequestration within water bodies (Regnier et al., 2013).

DOC and POC in lentic waters are of primary importance in terms of water quality. DOC absorbs light and may inhibit photosynthesis (Karlsson et al., 2009). This affects dissolved oxygen (DO) and DIC dynamics (Blough, 2001; Schindler, 2004). In many cases, DOC can also cause browning of waters that associates with numerous economic disadvantages. In waters used for drinking water supply, elevated DOC contents do not only pose aesthetic concerns.

~~For instance,~~but for instance, DOC reactions with chlorine during disinfection can produce numerous harmful by-products during water treatment (Karst et al., 2004; Bond et al., 2014; Fisher et al., 2017). Therefore, the evaluation of OM turnover, especially with respect to DOC, is of critical importance for water quality management of surface waters used for drinking water production. On the other hand, the rate of POC turnover may also affect sedimentation rates and therefore control the amounts of carbon deposited in sediments (Azam et al., 1983; Keaveney et al., 2020). ~~This may~~Such carbon accumulation may then lead to excessive losses of methane from lentic water bodies, which is relevant for greenhouse gas production (Bastviken et al., 2010; Huang et al., 2019; Jansen et al., 2022).

~~Also~~In addition, ~~the~~ mineralisation of OM into DIC has implications on greenhouse gas dynamics as it releases CO_2 into the water, a process that also ~~, thus causing~~ increases ~~in~~ DIC (Sun et al., 2016). In lakes that are poorly affected by inorganic carbon sequestration processes such as photosynthesis or calcite precipitation (Khan et al., 2022), increases of DIC concentrations may lead to CO_2 degassing from the water column. From this perspective, lentic water bodies are not only reactors for carbon turnover but also sources of CO_2 (Åberg et al., 2004; Cole et al, 2007). This highlights the need for aqueous studies with closer investigation ~~that investigate~~ of OM contributions to the DIC pool. ~~in aqueous systems.~~

Carbon turnover in aqueous systems can be investigated by means of concentrations and carbon stable isotopes ($\delta^{13}C$) of DIC, DOC, and POC (MacKenzie et al., 2004; Schulte et al., 2011; van Geldern et al., 2015). A common scheme is that respiration causes ~~simultaneous~~ decreases of $\delta^{13}C_{DIC}$ ~~with~~ that associate with increases of DIC concentrations in water (Stiller and Nissenbaum, 1999; Gammons et al., 2014). Such $\delta^{13}C_{DIC}$ decreases ~~This is~~ relate~~d~~ to the fact that the processed OM is usually enriched in ^{12}C ~~enriched~~ and therefore has more negative $\delta^{13}C$ values when compared to its inorganic counterparts. During OM degradation, this more negative isotope signal ~~is~~ becomes transferred to the DIC pool. Therefore, mass balances that combine carbon concentration data with isotopes may serve as useful ~~tools~~ source tracers ~~for~~ in~~the study~~ studies of aqueous carbon turnover ~~in aqueous systems~~ (Barth et al., 2017).

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In this study, ~~We~~ we investigated the turnover of OM into DIC with data from the ~~temperate~~ Rappbode Reservoir, that is Germany´s largest drinking water reservoir ~~in Germany~~. ~~With this, we~~Our principal aim was~~ed~~ to constrain preferential turnover of ~~one or~~ of the various sources of POC (allochtonous, autochtonous, sedimentary) or DOC. A further objective was to define turnover rates and to outline in which compartments of the reservoir they might be ~~highest~~most pronounced. We also applied this approach to a Metalimnetic Oxygen Minimum (MOM) in the reservoir. Here, carbon turnover may be even more pronounced as it is known for its strong depletion in dissolved oxygen (Shapiro, 1960; Nix, 1981; Kreling et al., 2017; Dordoni et al., 2022). The Rappbode Reservoir ~~was~~ offered an ideal location for this study because in recent years its logistic settings helped to develop it into an increasingly acknowledged large-scale laboratory of ecological behaviour for man-made lentic water bodies (Kong et al., 2019; Wentzky et al., 2019; Herzsprung et al., 2020; Mi et al., 2020).

2~~.~~ Methods

The Rappbode Reservoir in the Harz Mountains ~~is the largest drinking water reservoir in Germany, with~~has a surface area of 3.9 km^2 and a maximum depth up to 90 m. ~~a~~Its- maximum volume ~~of~~can reach up to 0.113 km^3. The reservoir

~~also has considerable importance~~also produces ~~for~~ hydropower ~~production~~ (Rinke et al., 2013). It receives water from two streams, the Hassel and the Rappbode. Two pre-reservoirs with a total volume < 0.002 km^3 are set on the path of these two rivers and are described in detail by Friese et al. (2014). Another input to the Rappbode Reservoir is an artificial water transfer gallery from the Königshütte Reservoir. The ~~M~~mixing season at Rappbode Reservoir normally ~~u~~occours ~~years~~ between the beginning of December and ~~the beginning of April~~the middle of March. Complete stratification is visible from the end of May, and boundaries between the epilimnion, metalimnion, and hypolimnion usually perstist until middle November (cf~~r~~ supplementary material S1, Fig. S1). During the stratification period, the compartments act as close systems and evolve independently from each other ~~during the stratification~~ season. For example, dissolved oxygen (DO) can hardly exchange between the different parts of the reservoir and its concentrations are higher in the epilimnion due to biota developments in spring and summer and related photosynthetic production of O_2 (Wentzky et al., 2019). On the other hand, respiration dominates the metalimnion and hypolimnion of the reservoir at different degrees (Dordoni et al., 2022).

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Sampling campaigns at the Rappbode Reservoir were carried out between March 2020 and December 2020 at a central location of the water body (51° 44´ 19” N, 10° 53´ 30” E, 420 m a.s.l.; Fig. 1). This monitoring station is located at a distance of around 515 meters from the main dam and is ~~represent the most illustrative~~ the best representative point of the reservoir for ~~the~~ processes ~~occurring~~ in the water column ~~of the reservoir~~. Sampling campaigns took place at least every two weeks. For this work, we investigated depths at 13, 16, 22, 40 and 65 meters below the water surface. Samples were collected with a LIMNOS-Watersampler^{TM} (HYDRO-BIOS) in 1-~~–~~L airtight amber-glass borosilicate bottles (DURAN^{TM}). They were prepared for laboratory analyses within one hour after sampling.

In the field, measurements of temperature and pH were performed on each depth-specific sample by a digital multi-parameter instrument (HQ40d; Hach Company, Loveland, CO, U.S.A.). Water samples for dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) were filtered through 0.45 µm pore-size syringe disk filters (Minisart HighFlow PES, Sartorius AG, Germany) into 40-mL amber-glass vials that were closed airtight by butyl rubber septa. These vessels conform to US Envrionmental Protection Agency (EPA) standards and were pre-poisoned with 20 µL of a supersaturated mercuric chloride ($HgCl_2$) solution to avoid secondary microbial activities after sampling. Duplicate samples were stored in the dark at 4 °C.

In the laboratory, water samples were analyzed for carbon stable isotopes of DIC ($\delta^{13}C_{DIC}$) and DOC ($\delta^{13}C_{DOC}$) by an Aurora 1030W TIC-TOC analyzer (OI Analytical, College Station, Texas) that was coupled in continuous flow mode to a Thermo Scientific Delta V plus isotope ratio mass spectrometer (IRMS). Concentrations were determined from the signal of the OI internal non-dispersive infrared sensor (NDIR) and a set of calibration standards. All stable isotope values in our work are reported as δ-notations in per mille (‰) versus the standard reference for carbon isotopes (Vienna Pee Dee Belemnite – VPDB) according to:

$$\delta = [(R_{sample} / R_{reference}) - 1] * 1000 \qquad (1)$$

where R is the molar ratio of the heavy and light carbon isotopes~~ (i.e. $^{13}C/^{12}C$)~~. ~~These results were multiplied by 1000 to express them in per mille (‰).~~ Standard deviations of both $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$ measurements were better than ± 0.3 ‰ (1-σ).

Particulate organic carbon (auto-POC) from water samples was collected on pre-heated (400°C) glass fibre filters (GFF) with a pore size of 0.4 µm (Macherey Nagel GF-5). The GFF were freeze-dried and subsequently pulverized using a ball mill (Retsch CryoMill). The resulting powder was fumigated by concentrated HCl in a desiccator for 24 hours to eliminate possible carbonate particles on the filters. Afterwards, the sample was stored for 1 hour at 50 °C to allow degassing remaining acid fumes. Grinded and de-calcified GFF sample material was then weighed into tin capsules for isotope analyses. Samples were analyzed for their $\delta^{13}\mathrm{C}_{\text{auto-P}}$~~$_{\mathrm{P}}$~~$_{\mathrm{OC}}$ signals using a Costech Elemental Analyzer (ECS 4010; Costech International, Pioltello, Italy; now NC Technologies, Bussero, Italy) in continuous flow mode coupled to a Thermo Scientific Delta V plus isotope ratio mass spectrometer (ThermoFisher Scientific, Bremen, Germany). The standard deviation of these measurements was was better than ± 0.3 ‰ (1-σ).

The vertical division of the water column into the compartments (epilimnion, metalimnion and hypolimnion) was arranged according to temperature data (supplementary material S1, Fig. S1).

The mass balance for carbon turnover calculations ~~only~~ works ~~for~~ best in environments where respiration is the dominant process. This is because in the epilimnion the $\delta^{13}C_{DIC}$ signal is also influenced by photosynthesis~~,~~ and ~~also~~ by degassing of CO_2 to the atmosphere. Both ~~these~~ processes shift the $\delta^{13}C_{DIC}$ values towards more positive values in patterns that are difficult to predict and depend on the type of algae community and magnitudes of CO_2 degassing. These uncertainties render a closed mass balance approach difficult for the epilimnion (Barth et al., 1998; van Geldern et al., 2015). Therefore, we restricted mass balance calculations for OM turnover to the metalimnion and the hypolimnion. The isotope mass balance equation relies on the determination of molar contibutions from OM to DIC pool as follows:

$$n_{fromOM} = n_t \times \frac{(\delta^{13}C_t - \delta^{13}C_s)}{(\delta^{13}C_s - \delta^{13}C_{OM})} \qquad (2)$$

where

n_{fromOM} is the molar C-contribution of OM to the DIC pool

n_t is the molar concentration of the DIC at the time when the water column was homogenised by the lake turnover at the beginning of the year (time 0, i.e. 17 March 2020)

~~and~~

$\delta^{13}C_t$ is its ~~correspondant~~ corresponding carbon isotope composition

$\delta^{13}C_s$ is the isotope composition of DIC of any sampling event later than time 0

$\delta^{13}C_{OM}$ is the isotope composition of the considered OM source material that ~~was~~ may have been turned into DIC.

Further details regarding equation (2) are provided in the supplementary material S1.

The organic matter (OM) sources ~~that we~~ studied were DOC, auto-POC, SED and particulate organic carbon of allochthonous origin (allo-~~Ext~~POC). Their individual carbon isotope compositions ($\delta^{13}C_{OM}$) ~~was~~ were the variable that was replaced for each sample calculation in equation (2). We used field data for all the variables of the equation, except for $\delta^{13}C_{SED}$ and $\delta^{13}C_{allo-}$~~$_{Ext}$~~POC. For $\delta^{13}C_{SED}$~~the latter two~~, we used data from relevant ~~the~~ literature sources that corresponded to -~~30~~31.~~7~~1 ‰ (Liu et al., 2022). As for $\delta^{13}C_{allo-POC}$, we used a range of values between ~~and~~ -31.8 ‰ and -28.6 ‰~~, respectively~~ that were retrieved from the literature ~~(Barth et al., 2017)~~(Tittel et al., 2019) and from 18 unpublished data points from entering rivers that were provided by the Helmholtz Zentrum für Umweltforschung~~zentrum~~ in Magdeburg. These data were measured in 2020, however because we did no sample them in the same frequency as the water samples from the reservoir and because they are likely less variable we think that they are tranferable to our study.~~.~~ One requirement for using this method is the increase in DIC from time 0 to each subsequent sampling event.

We also tested the validity of equation (2) via an error propagation approach (Ku, 1966; Kretz, 1985):

$$S = \sqrt{\left(\frac{\partial n_{fromOM}}{\partial n_t}\right)^2 \cdot sn_t{}^2 + \left(\frac{\partial n_{fromOM}}{\partial \delta^{13}C_t}\right)^2 \cdot s\delta^{13}C_t{}^2 + \left(\frac{\partial n_{fromOM}}{\partial \delta^{13}C_s}\right)^2 \cdot s\delta^{13}C_s{}^2 + \left(\frac{\partial n_{fromOM}}{\partial \delta^{13}C_{OM}}\right)^2 \cdot s\delta^{13}C_{OM}{}^2} \qquad (3)$$

Where S is the total standard variation and s refers to the standard variation of each sampling date. More information about this method is available in the supplementary material~~S1~~.

The evaluation of OM turnover into the DIC pool is limited to the ~~lower~~ metalimnion and the hypolimnion of the Rappbode Reservoir because only in these zones we obtained a good correlation between DIC and its isotopes (supplementary material S1, Fig. S2). For comparison to the isotope mass balance (Eq. 2) we also determined DIC gains with concentration differences from time 0 (n_{s-t}). Here we aimed to ~~study~~ find out which correlations would be closest to a 1:1 line in order to narrow down the most plausibel source of OM turnover.

We also calculated OM to DIC turnover rates in the metalimnion and in the hypolimnion. For ~~the~~ considerations of the metalimnion, we additionally separated the layer showing the minimal oxygen concentration (Metalimnetic Oxygen Minimum, MOM)~~and calculated MOM-specific turnover rates~~. Our results are expressed in µmol L^{-1} d^{-1} for individual sampling dates with their time differences between time 0 (17 March 2020) up to a maximum of 259 days (i.e. 08 December 2020). In order to evaluate OM seasonal turnover rates, we subdivided our database ~~according to~~following Wang et al. (2021). According to this scheme, ~~Spring~~ spring ranged from 17 February to 11 June, summer from 12 June to 14 September, autumn from 15 September to 5 December and winter from 6 December to 16 February.

~~3. Results~~

~~Figure 2 shows DIC profiles within the studied time period divided into seasons. DIC concentrations generally increased from 17 March 2020 (time 0) over the course of the study period. The spring profiles showed the smallest range of DIC concentrations (0.29 mmol L-1 to 0.36 mmol L-1). Concentration differences between depth profiles were smallest in summer. However, they showed a pronouced increase in DIC concentration with respect to time 0, with~~

~~values ranging from 0.33 to 0.58 mmol L^{-1} (Fig. 2). A sample from 22 meters depth on 04/08/2020 had an exceptional high DIC content, whereas one DIC decrease was recorded at 16 meters depth on the 18/04/2020.~~

~~Concentration differences between depth profiles were smallest in summer. However, they showed a pronouced increase in DIC concentration with respect to time 0, with values ranging from 0.33 to 0.58 mmol L^{-1} (Fig. 2). A sample from 22 meters depth on 04/08/2020 had an exceptional high DIC content, whereas one DIC decrease was recorded at 16 meters depth on the 18/04/2020.~~

~~Samples from autumn had the highest DIC concentrations with values between 0.38 and 0.59 mmol L^{-1} (Fig. 2). A noteworthy feature for autumn and winter was the presence of very high DIC concentrations in samples from 13 and 16 metres depth on 29/09/2020. They showed values of 1.00 and 0.94 mmol L^{-1}, respectively (Fig. 2).~~

~~For comparison to the isotope mass balance (Eq. 2) we also determined DIC gains with concentration differences from time 0 (n_{s-t}). These results were plotted against the DIC concentration gains as calculated by equation (2) (Fig. 3). With this analysis, in situ produced POC showed the best linear regression that was closest to a 1:1 line (Tab. 1). This was even clearer when only the hypolimnion was considered, with an angular coefficient of the regression line for POC being 1.00. On the other hand, in the metalimnion the angular coefficient for DOC was reasonably close to the one of POC with values of 1.15 and 1.12, respectively. The MOM was considered separately and also showed a clear predominance of POC input as the OM sources with an angular coefficient of 1.05.~~

~~DIC production rates from POC turnover as the dominant OM input in the water column of the Rappbode Reservoir are reported in figure 4. They ranged from 0.1 to 1.3 µmol L^{-1} d^{-1}. The metalimnion and the upper part of the hypolimnion showed higher rates, up to 1.3 µmol L^{-1} d^{-1}. The metalimnion showed less variations than the hypolimnion and ranged from 0.3 to 1.1 µmol L^{-1} d^{-1}. The highest DIC production rates were found among the MOM samples, which complies with the fact that oxygen depletion is most intense in this layer. DIC rates for the hypolimnion ranged from 0.1 to 1.3 µmol L^{-1} d^{-1}, with the highest variance at a water depth of 22 meters (0.2 to 1.3 µmol L^{-1} d^{-1}). Samples from 40 m depth had the lowest DIC productivity with values below 0.2 µmol L^{-1} d^{-1}. With one exception at 40 m depth, data from 65 meters depth had higher rates but covered a narrower range of variation (0.5 to 0.7 µmol L^{-1} d^{-1}).~~

~~Data from springtime had the highest spread of POC turnover rates for each depth except for 13 meters. In this depth, MOM waters exceeded the springtime range of variation. Also, samples from summer and autumn showed higher turnover rates than those of spring. Overall, the highest carbon turnorver rates to DIC were found in springtime and during summer, when the MOM developed. The complete database is available in the supplementary material.~~

3~~4.~~ Results and Discussion

3.1 Dissolved inorganic carbon concentrations

Figure 2 shows DIC profiles within the studied time period divided into seasons. DIC concentrations generally increased from 17 March 2020 (time 0) over the course of the study period. The spring profiles showed the smallest range of DIC concentrations (0.29 mmol L^{-1} to 0.36 mmol L^{-1})~~.At the Rappbode Reservoir, DIC concentrations~~ and an overall homogeneity througout the water column ~~were almost homogeneous during the mixing period.~~. This is in accordance with the theory of biogeochemical uniformity during and shortly after mixing periods of lentic water bodies (Wetzel, 1984). DIC values at this starting point were lower when compared to subsequently collected samples. This was related to ~~because the water column was closest to~~ an overall equilibration with the atmosphere. ~~and~~In addition, due to lower temperatures, metabolic processes were still low. Concentration differences between the different depth profiles that were collected fortnightly were smallest in summer. However, they showed a pronouced increase in DIC concentration with respect to time 0, with values ranging from 0.33 to 0.58 mmol L^{-1} (Fig. 2). A sample from 22 meters depth on 04/08/2020 had an exceptional high DIC content, whereas one exceptional DIC decrease was recorded at 16 meters depth on 18/04/2020. Samples from autumn had the highest DIC concentrations with values between 0.38 and 0.59 mmol L^{-1} (Fig. 2). Note that, in autumn and winter, samples from 13 and 16 metres depth had very high DIC concentrations in ~~samples from 13 and 16 metres depth were found~~. They showed values of 1.00 and 0.94 mmol L^{-1}, respectively (Fig. 2).~~The~~ Overall, ~~T~~these ~~following~~ continuous increases ~~-~~of DIC below the photic zone in the metalimnion and the hypolimnion with time are most plausibly due to respiration ~~and to reduced exchanges between the compartments due to stratification~~and associated turnover of OM. ~~This~~ Logically effects of respiration can best be shown in the hypolimnnion, where the counteracting effects of photosynthesis and CO_2 degassing (processes that both reduce DIC contents) are minimal.

DIC concentration increases near the bottom of the lake (65 m) ~~are usually~~may also be related ~~-attributed~~ to contributions from processes involving organic turnover within the sediments (Wetzel, 1984). On the other hand, higher DIC concentrations found in the metalimnion are related to respiration processes that link to OM input from above. Not~~ably~~e that~~,~~ the MOM samples had the highest DIC concentrations, with values up to 1 mmol L^{-1}. This matches ~~the~~ with findings ~~of~~ by Giling et al. (2017) who also found that the metalimnion may act as a ~~deicisive~~ metabolic hospot in oligotrophic water bodies. Additionally, MOM samples also had the highest auto-POC and DOC concentrations (cf supplementary material S2), which commonly mark zones close to phytoplankton assemblages (Wetzel et al., 1972). ~~This is a typical scenario~~Such high OM concentrations may indicate ~~after~~ the collapse of an algae bloom, when settling detritus becomes directly subject to decomposition and accelerates respiratory turnover. This hypothesis is supported by our data that show predominant autochthonous POC consumption. Temperature-related viscosity changes that are typical of the metalimnion may also have enhanced the residence time of organic matter. Altogether, these findings suggest a relation between the MOM and a productive biotic assemblage in vertical proximity above the MOM. This connection is also supported by data from the literature (Kreling et al., 2017; McDonald et al., 2022) and was already highlighted independently by previous studies with dissolved oxygen isotope insights on the Rappbode Reservoir (Dordoni et al., 2022).

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3.2 Carbon stable isotopes of organic matter and its mineralization

3.2.1 Epilimnion

It was not possible to evaluate OM contributions to the DIC pool for the epilimnion because no reasonable correlation between DIC concentration and its isotopes was found in this compartment (supplementary material S1, Fig. S2). Although previous studies reported that respiration tends to exceed photosynthesis in the epilimnion of oligothrophic water bodies (del Giorgio and Peters, 1993; del Giorgio et al., 1997; Duarte and Agustí, 1998), this result was expected due to the intense influence of photosynthesis and CO_2 degassing to the atmosphere on $\delta^{13}C_{DIC}$. On the one hand, photosynthesis generates more positive $\delta^{13}C_{DIC}$ values (Ahad et al., 2008; Wachniew, 2006; Gammons et al., 2011). ~~On the other,~~These shifts~~ of~~ of $\delta^{13}C_{DIC}$ signals towards more positive values~~, an effect that~~ can also result from CO_2 degassing to the atmosphere. Therefore, OM turnover calculations could not be corrected for these counteracting and less systematic effects. Nonetheless, it is likely that OM turnover rates in the epiliminion ~~are higher than~~are at least as high as in ~~the other two compartments~~the Metalimnion and Hypolimnion because the photic zone directly offers fresh authochtonous POC material for turnover.

3.2.2 Metalimnion, MOM and hypolimnion

~~$\delta^{13}C_{DOC}$ v~~Variations of $\delta^{13}C_{DOC}$ during our observation period were small and ranged from -28.8 ‰ to -27.1 ‰ (Fig. 3). Instead, changes in $\delta^{13}C_{auto\text{-}POC}$ followed the development of stratification, with the mixing period characterized by lower values (down to -36 ‰ in the upper part of the water column). On the other hand, ~~the stratification period showed~~ we also found higher $\delta^{13}C_{auto\text{-}POC}$ that reached values ~~over~~ higher than -24.0 ‰ around 16 meters depth at the end of August 2020 (Fig. 3). This ~~setup~~range ~~is probably~~likely ~~closely linked to the~~indicates developments of different species of biota in the water column during the year~~, which have~~ with different $\delta^{13}C_{auto\text{-}POC}$. ~~Given the range of depths studied, it is reasonable to assume that the alga that primarily influences these fluctuations~~In the MOM zone a likley species is the cyanobacterium *Planktothrix rubesces*. This type of cyanobacterium finds an optimum at metalimnetic depths (Nürnberg et al., 2003; Gisriel et al., 2020). Its blooms in the metalimnion of Rappbode Reservoir from late summer to autumn are well documented (Wentzky et al., 2019).

In order to evaluate OM contributions to the DIC pool, we determined DIC gains with concentration differences from time 0 ($n_{s\text{-}t}$) and compared them to DIC concentration gains as calculated via the isotope mass balance ~~by~~ (~~equation~~eq. (2) (Fig. 4). With this analysis, results with input from auto-POC showed the best linear regression that was closest to a 1:1 line (Tab. 1). This was ~~even clearer~~most obvious when only the hypolimnion was considered, with an angular coefficient of the regression line for auto-POC being 1.00. Note that the green zone in Fig. 4 marks the minimum and maximum $\delta^{13}C$ values of the allo-POC. This shows that in the metalimnion and the MOM zone a clear differentiation between allo- and auto-POC is not possible any more. Nonetheless in the MOM zone the line for allo-POC and DOC are closest to the 1:1 line. Overall even though a clear differentiation between auto and allo POC turnover in the Metalimnion was not possible it is still likely that also in this zone auto-POC is the main contributor to DIC increases. This is supported by the clear signal from the Hypolimnion and the fact that the Metalimnion is the zone that receives most of the freshly produced OM that mostly consists of auto-POC. Except for samples at the bottom it is also unlikely

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the sedimentary OM influced DIC increases in the entire water column above. ~~On the other hand, in the metalimnion the angular coefficient for DOC was reasonably close to the one of auto-POC with values of 1.15 and 1.12, respectively. Note that regressions for the metalimnion~~This~~ also leaves room for uncertaint~~ies~~y (Table 1). This is becauselikely due to the fact that the photic zone at the Rappbode Reservoir can extend down to metalimnetic depths, where residual influences of photosynthesis may complicate the relationships between OM and DIC as described for the epilimnion. The MOM was considered separately from the metalimnion and also showed a clear predominance of auto-POC input as the OM sources with an angular coefficient of 1.05. Overall, this good fit between DIC differences and isotope mass balances with auto-POC serves as a good indication that auto-POC is indeed the most favorable OM used for respiratory turnover into DIC.~~

~~It was not possible to evaluate OM contributions to the DIC pool for the epilimnion because no reasonable correlation between DIC concentration and its isotopes was found in this compartment (supplementary material, Fig. S2). Although previous studies reported that respiration tends to exceed photosynthesis in the epilimnion of oligothrophic water bodies (del Giorgio and Peters, 1993; del Giorgio et al., 1997; Duarte and Agustí, 1998), this result was expected due to the intense influence of photosynthesis and CO~~$_2$~~ degassing to the atmosphere on ~~$\delta^{13}C_{DIC}$~~. On the one hand, photosynthesis generates more positive ~~$\delta^{13}C_{DIC}$~~ values (Ahad et al., 2008; Wachniew, 2006; Gammons et al., 2011). On the other, shifts of ~~$\delta^{13}C_{DIC}$~~ towards more positive values also result from CO~~$_2$~~ degassing to the atmosphere. Therefore, OM turnover calculations could not be corrected for these counteracting and less systematic effects. Nonetheless, it is likely that OM turnover rates in the epiliminion are higher than in the other two compartments because the photic zone directly offers fresh authochtonous POC material for turnover.~~

~~Note that regressions for the metalimnion also leaves room for uncertainty (Table 1). This is because the photic zone at the Rappbode Reservoir can extend down to metalimnetic depths, where residual influences of photosynthesis may complicate the relationships between OM and DIC as described for the epilimnion.~~

~~The isotope approach used to assess the turonver of OM within the metalimnion and the hypolimnion of the Rappbode Reservoir confirmed that POC is the main OM contributor to the DIC pool. This was shown by the closest fit to the 1:1 line of the correlation between DIC gains as calculated from differences between DIC concentration from 17 March 2020 (time 0) and each sampling event and the results from the mass balance in equation (2). This good fit serves as a good indication that autochthonous POC is indeed the most favorable OM used for respiratory turnover into DIC.~~

Calculation-related uncertainties may have been higher when we used average $\delta^{13}C$ input values of SED and allo-~~Ext~~POC from the literature without any variance to constrain their contribution to the DIC pool. This is because neither sedimentary material nor allo-POC were sampled in a fortnightly interval over the observation period. ~~However, in~~As a substitute for these ~~the absence of~~ field data that ~~,~~ we used $\delta^{13}C_{allo\text{-}POC}$ data from Rappbode inputs that were made available by the Helmholtz Centre for Environmental research (UFZ). ~~We hence believe that our~~With expected little carbon isotope variation of these two OM pools our approximation should be sufficient to provide ~~an accurate~~a plausible ~~estimation~~evaluation.

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~~The~~One reason why allochtonous-related OM does not seem to contribute significantly to the DIC pool in the reservoir might be that its mass is insufficient to exert enough impact on the ~~whole~~ entire carbon budget. This suggests either low inputs from the tributaries and the catchment or low turnover of this carbon phase within the reservoir. The latter option is more plausible as POC concentrations were often higher than expected by autochtonous POC concentrations and reached values of up to 1.05 mg L^{-1} (supplementary material S2). In addition the averages of $\delta^{13}C_{allo\text{-}POC}$ and $\delta^{13}C_{SED}$ are very close with values of -30.6 ‰ and -31.1 ‰. This is another indication that most of the allo-POC reaches the sedimentary pool with little or no further processing. ~~Carbon isotope compositions for auto-POC and allo-POC overlap for few metalimnetic samples between March and May. This is an additional reason why we were not able to constrain a definite OM source for DIC pool in the metalimnion. For the remaining data in the database, isotope compositions for auto-POC and allo-POC differed enough to differentiate these sources.~~

Despite its high concentrations in the water column, the influence of DOC ~~seemed to have~~may also have had secondary influences on DIC increases. This was obvious by the regression lines in Fig.4. Although studies on rivers have proven that DOC can fuel metabolic processes in peat-dominated heterotrophic ecosystems (Thurman, 1985; Billett et al., 2010), the DOC pool in lentic oligotrophic water bodies consists primarily of carbon compounds that are older and more resistant to bacterial decomposition (Wetzel, 1984). As a result, bacteria prefentially consume autochthonous POC that consists mainly of fresh material (Cole et al., 1984; Barth et al., 2017). Note, however, that if part of the DOC pool found in the Rappbode reservoir resulted from leaching of auto-POC, it should have the same isotope composition as the original POC material itself. If this part of the DOC pool ~~became~~ becomes turned over into DIC by respiration, we would not be able to differentiate from a direct auto-POC input.

3.3 Turnover rates

DIC production rates from auto-POC turnover as the dominant OM input in the water column of the Rappbode Reservoir are reported in figure 5. They ranged from 0.1 to 1.3 µmol L^{-1} d^{-1} and were ~~Overall, OM turnover rates into DIC were~~ comparable to those found in other oligotrophic water bodies (Cole et al., 1984; Scavia and Laird, 1987; Carignan et al., 2000; Lammers et al., 2017). Therefore, our results seem to successfully approximate the expected ~~setup~~carbon processing of the aquatic environment and could be used as an alternative approach to quantify turnover rates of OM without the use of in situ incubation experiments.

Data from the~~The~~ metalimnion and the upper part of the hypolimnion showed higher turnover rates of up to 1.3 µmol L^{-1} d^{-1}. The metalimnion showed less variations than the hypolimnion and ranged from 0.3 to 1.1 µmol L^{-1} d^{-1}. The highest DIC production rates were found ~~among~~within the MOM samples. This observation matches with the fact that oxygen depletion is most intense in this layer (Dordoni et al., 2022). DIC production rates for the hypolimnion ranged from 0.1 to 1.3 µmol L^{-1} d^{-1}, with the highest variance at a water depth of 22 meters (0.2 to 1.3 µmol L^{-1} d^{-1}). Samples from 40 m depth had the lowest DIC productivity with values below 0.2 µmol L^{-1} d^{-1}. Higher rates of auto-POC turnover above 23 meters depth in ~~figure 5~~ may have been caused by higher availabilities of fresh auto-POC produced by photosynthesis within the photic zone. This also indicates that OM turnover in this part of the water column depends largely on freshly produced auto-POC material that sinks downward and may decompose more rapidly due to high

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oxygen availability (Pace and Prairie, 2005). This concept agrees with the appearance of epilimnetic diatom blooms in early spring and with phytoplankton blooms in the metalimnion of the Rappbode Reservoir from summer to early autumn (Wentzky et al., 2019). This explanation likely also applies to samples from a water depth of 40 metres, where the rate of respiratory carbon turnover depends primarily on the residence time of OM (Robarts, 1986). In support of this explanation, summer and autumn turnover rates of our study are higher than the spring ones particularly at this depth (Fig. 5). With one exception at 40 m depth, data from 65 meters depth had higher rates but covered a narrower range of variation (0.5 to 0.7 µmol L^{-1} d^{-1}). Increased turnover rates for ~~samples from 65 meters~~this depth may appear as a contradiction. However, ~~S~~such values likely result from detritus decomposition with carbon contributions from the sediments.

Turnover rtates from springtime had the highest spread of auto-POC turnover rates for each depth except for 13 meters. At this depth, MOM waters exceeded the springtime range of variation. Samples from summer and autumn showed higher turnover rates than those of spring. Overall, the highest carbon turnorver rates to DIC were found in springtime and during summer, when the MOM developed. The complete database is available in the supplementary material S2. ~~Overall, t~~The reason why spring turnover values are generally lower may ~~lie in the~~relate to combined effects of temperature, residence time~~,~~ and nature of decomposing detritus. During springtime, most of the organic matter derived from diatom blooms is sequestered within the epilimnion (Sommer et al., 1986) and the amount of detritus that can reach greater depths to become mineralized is low. Additionally,~~ the~~ heavy silica shells of diatoms decrease their residence time in the water column. Moreover, cold temperatures in spring reduce mineralisation rates.

~~Overall, OM turnover rates into DIC were comparable to those found in other oligotrophic water bodies (Cole et al., 1984; Scavia and Laird, 1987; Carignan et al., 2000; Lammers et al., 2017). Therefore, our results seem to successfully approximate the expected setup of the aquatic environment and could be used as an alternative approach to quantify turnover rates of OM without the use of in situ incubation experiments.~~

~~Higher rates of POC turnover above 23 meters depth in figure 4 may have been caused by higher availabilities of POC produced by photosynthesis within the photic zone. This also indicates that OM turnover in this part of the water column depends largely on freshly produced POC material that sinks downward and may decompose more rapidly due to high oxygen availability (Pace and Prairie, 2005). This is in agreement with the appearance of epilimnetic diatom blooms in early spring and phytoplankton blooms in the metalimnion of the Rappbode Reservoir from summer to early autumn (Wentzky et al., 2019). This explanation likely also applies to samples from a water depth of 40 metres, where the rate of respiratory carbon turnover depends primarily on the residence time of the detritus (Robarts, 1986). In support of this explanation, summer and autumn turnover rates are higher than the spring ones particularly at this depth (Fig. 4). Increased turnover rates for samples from 65 meters depth may appear as a contradiction. Such values likely result from detritus decomposition with carbon contributions from the sediments. Overall, the reason why spring turnover values are generally lower may lie in the combined effects of temperature, residence time, and nature of decomposing detritus. During springtime, most of the organic matter derived from diatom blooms is sequestered within the epilimnion (Sommer et al., 1986) and the amount of detritus that can reach greater depths to~~

~~become mineralized is low. Additionally, the heavy silica shells of diatoms decrease their residence time in the water column. Moreover, cold temperatures in spring reduce mineralisation rates.~~

Unlike the the rest of the metalimnion, MOM samples hardly seem to be influenced by photosynthesis and show a clear predominance of respiration. Also in this zone auto-POC was determined as the main contributor to the DIC pool, with turnover rates that ~~are the~~were highest for summertime and among the highest in the whole database (Fig. ~~5~~4). Once again, this result suggests close relationships between metabolism of the auctochtonous phytoplankton community and its decay and the following emergence of the MOM (Shapiro, 1960). This finding also supports the interpretations by Kreling et al. (2017) and McDonald et al. (2022) of downward fluxes of POC ~~promoting~~ that promote the development of MOM. Overall, our study agrees with preliminary studies on the pre-reservoir dams in the Rappbode System (Barth et al., 2017). This suggests that similar OM turnover principles apply despite volume differences between the main water body and its pre-reservoirs.

~~Overall, our study agrees with preliminary studies on the pre-reservoir dams in the Rappbode System (Barth et al., 2017). This suggests that similar OM turnover principles apply despite volume differences between the main water body and its pre-reservoirs.~~

~~5.~~4 Conclusions

Comparisons between DIC concentration differences and stable carbon isotope mass balances of OM turnover in an oligotrophic drinking water reservoir demonstrated dominant turnover of freshly produced auto-POC. DOC turnover seemed negligible, unless part of this pool was generated by leaching from the auto-POC pool. This sort of DOC would be isotopically identical to its precursor POC material.

Calculated rates of auto-POC turnover into DIC by respiration are typical of oligotrophic water bodies and could be assessed with our method without the use of in situ incubation experiments. Therefore, our approach may provide a promising alternative to complex incubation experiments. Nevertheless, such findings based on isotope mass balances should be tested in parallel with data from incubations to evaluate and narrow down uncertainties.

~~Especially~~ When ~~low~~ turnover rates are low, this is a good ~~indicate~~ indication of the environmental fragility of the Rappbode Reservoir. FOr instance, such fragilities mean~~This shows~~ that if large amounts of carbon were added to the system, it likely could transfer only part of this load into the DIC pool. Such a scenario could for instance occur with excessive algae blooms under ~~different~~ higher nutrient loads~~,~~ or ~~washing in of~~mobilisation of external ~~carbon~~ OM under different land use and climate conditions. In such a scenario, the current *in situ* respiration would likely be unable to cope with the excessive C loads. This would lead to higher sedimentation and water browning. Likely, such modifications of metabolic balances would also compromise the water quality. Overall, a comparison between DIC

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production rates with DO depletion rates as described by Dordoni et al. (2022) should be evaluated in order to prove the consistency of both isotope approaches. Such investigations will be subject of future studies.

The above considerations are ~~likely~~ well transferable to other temperate lentic systems, in which links between auto-POC turnover and associated DIC gains may operate under similar conditions but at different rates. ~~However~~Nonetheless, this study only focuse~~s~~d ~~on~~only on one single point with detailed depth profiles at high frequency. We therefore suggest that future studies should inquire spatial and lateral heterogeneities as well. Overall, our results may help to improve water management strategies to help foster economic and environmental management of drinking water reservoirs.

5~~6.~~ Data availability

Data are available in the supplementary material S2.

6~~7.~~ Author contribution

MD performed the formal analysis and was responsible for investigation, data curation and visualization. MD and JB cured the conceptualization, methodology, validation, resources, and writing of the original draft. MS, KR and RvG cured manuscript review and editing. KR and JB were responsible for project administration and funding acquisition. JB provided constant supervision.

7~~8.~~ Competing interests

The authors declare that they have no conflict of interest.

8~~9.~~ Acknowledgments

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9~~10.~~ References

Åberg, J., Bergström, A.-K., Algesten, G., Söderbackj, K., and Jansson, M.: A comparison of the carbon balances of a natural lake (L. Örträsket) and a hydroelectric reservoir (L. Skinnmuddselet) in northern Sweden. Water Res., 38, 531-538, doi:10.1016/j.watres.2003.10.035, 2004.

Ahad, J.M.E., Barth, J.A.C., Ganeshram, R.S., Spencer, R.G.M., and Uher, G.: Controls on carbon cycling in two contrasting temperate zone estuaries: The Tyne and Tweed, UK. Estuar. Coast. Shelf Sci., 78, 685-693, doi:10.1016/j.ecss.2008.02.006, 2008.

Azam, F., Fenchel, T., Field, J.G., Gray, J.S., Meyer-Reil, L.A., & Thingstad, F.: The Ecological Role of Water-Column Microbes in the Sea. Mar. Ecol. Prog. Ser., 10, 257-263, doi:10.3354/meps010257, 1983.

Barth, J. A. C., Veizer, J., and Mayer, B.: Origin of particulate organic carbon in the upper St. Lawrence: Isotopic constraints, Earth Planet. Sci. Lett., 162, 111-121, doi:10.1016/S0012-821X(98)00160-5, 1998.

Barth, J.A.C., Mader, M., Nenning, F., van Geldern, R. and Friese, K.: Stable isotopes mass balances versus concentration differences of dissolved inorganic carbon - implications for tracing carbon turnover in reservoirs. Isot. Environ. Health Stud., 53, doi:10.1080/10256016.2017.1282478, 2017.

Bastviken, D., Santoro, A. L., Marotta, H., Queiroz Pinho, L., Fernandes Calheiros, D., Crill, P., and Enrich-Prast, A.: Methane Emissions from Pantanal, South America, during the Low Water Season: Toward More Comprehensive Sampling. Environ. Sci. Technol., 44, 5450–5455, doi:10.1021/es1005048, 2010.

Billett, M.F., Charman, D.J., Clark, J.M., Evans, C.D., Evans, M.G., Ostle, N.J., Worrall, F., Burden, A., Dinsmore, K.J., Jones, T., McNamara, N.P., Parry, L., Rowson, J.G., and Rose, R.: Carbon balance of UK peatlands: current state of knowledge and future research challenges. Clim Res, 45,13-29, doi:10.3354/cr00903, 2010.

Blough, N.V.: Photochemical Processes. In: Encyclopedia of Ocean Sciences, doi:10.1006/rwos.2001.0072, 2001.

Bond, T., Huang, J., Graham, N. J. D., and Templeton, M. R.: Examining the interrelationship between DOC, bromide and chlorine dose on DBP formation in drinking water--a case study. Sci. Total Environ., 470-471, 469-479, doi:10.1016/j.scitotenv.2013.09.106, 2014.

Carignan, R., Planas, D., and Vis, C.: Planktonic production and respiration in oligotrophic Shield lakes. Limnol. Oceanogr., 45, 189–199, doi:10.4319/lo.2000.45.1.0189, 2000.

Cole, J.J., Likens, G. E., and Hobbie, J. E., 1984. Decomposition of planktonic algae in an oligotrophic lake. Oikos 42: 257-266, doi:10.2307/3544393

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Cole, J.J., and Prairie, Y.T.: Dissolved CO2 in Freshwater Systems. In: Reference Module in Earth Systems and Environmental Sciences, doi:10.1016/B978-0-12-409548-9.09399-4, 2014.

Downing, J.A., Middelburg, J.J., and Melack, J.: Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems, 10, 171–184, 2007.

Del Giorgio, P. A., and Peters, R. H.: The balance between phytoplankton production and plankton respiration in lakes. Can. J. Fish. Aquat. Sci., 50, 282–289, doi:10.1139/f93-032, 1993.

Del Giorgio, P. A., Cole, J. J., and Cimbleris, A.; Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems. Nature, 385, 148–150, doi:10.1038/385148a0, 1997.

DelSontro, T., Beaulieu, J. J., and Downing, J. A.: Greenhouse gas emissions from lakes and impoundments: Upscaling in the face of global change. Limnol. Oceanog. Lett., 3, 64–75, doi:10.1002/lol2.10073, 2018.

Dordoni, M., Seewald, M., Rinke, K., Schmidmeier, J., and M., Barth, J.A.C.: Novel evaluations of sources and sinks of dissolved oxygen via stable isotopes in lentic water bodies. Sci. Total Environ., 838, doi:10.1016/j.scitotenv.2022.156541, 2022.

Duarte, C. M., and Agustí, S.: The CO2 Balance of Unproductive Aquatic Ecosystems. Science, 281, doi:10.1126/science.281.5374.234, 1998.

Emerson, S.: Chemically enhanced CO2 gas exchange in a euthrophic lake: A general model. Limnol. Oceanog., 20, 743-753, doi:10.4319/lo.1975.20.5.0743, 1975.

Fisher, I. H., Kastl, G., and Sathasivan, A.: New model of chlorine-wall reaction for simulating chlorine concentration in drinking water distribution systems. Water Res., 125, 427-437, doi:10.1016/j.watres.2017.08.066, 2017.

Friese, K., Schultze, M., Böhrer, B., Büttner, O., Herzsprung, P., Koschorreck, M., Kuehn, B., Rönicke, H., Tittel, J., Wendt-Potthoff, K., Wollschläger, U., Dietze, M., and Rinke, K.: Ecological response of two hydro-morphological similar pre-dams to contrasting land-use in the Rappbode reservoir system (Germany). Int. Rev. ges. Hydrobiol. Hydrogr., 99, doi: 10.1002/iroh.201301672, 2014.

Gammons, C.H., Babcock, J.N., Parker, S.R., and Poulson, S.R.: Diel cycling and stable isotopes of dissolved oxygen, dissolved inorganic carbon, and nitrogenous species in a stream receiving treated municipal sewage. Chem. Geol., 283, 44-55, doi:10.1016/j.chemgeo.2010.07.006, 2011.

Gammons, C.H., Henne, W., Poulsom, S.R., Parker, S.R., Johnston, T.B., Dore, J.E., and Boyd, E.S.: Stable isotopes track biogeochemical processes under seasonal ice cover in a shallow, productive lake. Biogeochemistry, 120, 359-379, doi:10.1007/s10533-014-0005-z, 2014.

Gattuso, J.-P., Peduzzi, S., Pizay, M.-D., and Tonolla, M.: Changes in freshwater bacterial community composition during measurements of microbial and community respiration. J. Plankton Res., 24, 1197–1206, doi:10.1093/plankt/24.11.1197, 2002.

Giling, D. P., Staehr, P. A., Grossart, H. P., Andersen, M. R., Boehrer, B., Scot, C., Evrendilek, F., Gómez-Gener, L., Honti, M., Jones, I. D., Karakaya, N., Lass, A., Moreno-Ostos, E., Rinke, K., Scharfenberger, U., Schmidt, S. R., Weber, M., Woolway, R. I., Zwart, J. A., and Obrador, B.: Delving deeper: Metabolic processes in the metalimnion of stratified lakes. Limnol. Oceanogr., 62, 1288-1306, doi: 10.1002/lno.10504, 2017.

Gisriel, C., Shen, G., Kurashow, V., Ho, M.-Y., Zhang, S., Williams, D., Golbeck, J. H., Fromme, P., Bryant, D. A.: The structure of Photosystem I acclimated to far-red light illuminates an ecologically important acclimation process in photosynthesis. Sci. Adv. 6, doi: 10.1126/sciadv.aay6415, 2020.

Hanson, P.C., Bade, D.L., Carpenter, S.R., Kratz, T.K.: Lake metabolism: Relationships with dissolved organic carbon and phosphorus. Limnol. Oceanogr., 48, 1112-1119, doi:10.4319/lo.2003.48.3.1112, 2003.

Huang, C., Chen, Z., Gao, Y., Luo, Y., Huang, T., Zhu, A., Yang, H., and Yang, B.: Enhanced mineralization of sedimentary organic carbon induced by excess carbon from phytoplankton in a eutrophic plateau lake. J. Soils Sediments, 19, 2613–2623, doi:10.1007/s11368-019-02261-2, 2019.

Herzsprung, P., Wentzky, V., Kamjunke, N., von Tumpling, W., and Wilske, C.: Improved understanding of dissolved organic matter processing in freshwater using complementary experimental and machine learning approaches. Environ. Sci. Technol., 54, 13556 – 13565, doi:10.1021/acs.est.0c02383, 2020.

Jansen, J., Woolway, R. I., Kraemer, B. M., Albergel, C., Bastviken, D., Weyhenmeyer, G. A., Marcé, R., Sharma, S., Sobek, S., Tranvik, L. J., Perroud, M., Golub, M., Moore, T. N., Vinnå, L. R., La Fuente, S., Grant, L., Pierson, D. C., Thiery, W., and Jennings, E.: Global increase in methane production under future warming of lake bottom waters. Glob. Chang. Biol., doi:10.1111/gcb.16298, 2022.

Kawasaki, N., and Benner, R.: Bacterial release of dissolved organic matter during cell growth and decline: molecular origin and composition. Limnol. Oceanogr., 51, 2170–2180, doi:10.4319/lo.2006.51.5.2170, 2006.

Karlsson, J., Bystrom, P., Ask, J., Ask, P., Persson, L., and Jansson, M.: Light limitation of nutrient-poor lake ecosystems. Nature, 460, 506-509, doi:10.1038/nature08179, 2009.

Karst, G., Sathasivan, A., Fisher, I. H., and van Leeuwen, J.: Modeling DOC Removal by Enhanced Coagulation. J. Am. WATER Work. Assoc., 96,79-89, doi:10.1002/j.1551-8833.2004.tb10557.x, 2004.

Keaveney, E. M., Radbourne, A. D., McGowan, S., Ryves, D B., and Reimer, P. J.: Source and quantity of carbon influence its sequestration in Rostherne Mere (UK) sediment: a novel application of stepped combustion radiocarbon analysis. J. Paleolimnol., 64, 347–363, doi:10.1007/s10933-020-00141-1, 2020.

Kahn, H., Marcé, R., Laas, A., and Obrador, B.: The relevance of pelagic calcification in the global carbon budget of lakes and reservoirs. Limnetica, 41, 17:25, doi: 10.23818/limn.41.02, 2022.

Kong, X., Zhan, Q., Boehrer, B., Rinke, K.: High frequency data provide new insights into evaluating and modeling nitrogen retention in reservoirs. Water Res., 166, doi:10.1016/j.watres.2019.115017, 2019.

Koschorreck, M., Hentschel, I., and Boehrer, B.: Oxygen Ebullition From Lakes. Geophys. Res. Lett., 44, 9372-9378, doi:10.1002/2017GL074591, 2017.

Kreling, J., Bravidor, J., Engelhardt, C., Hupfer, M., Koschorreck, M., and Lorke, A.: The importance of physical transport and oxygen consumption for the development of a metalimnetic oxygen minimum in a lake. Limnol. Oceanogr., 62, 348-363, doi:10.1002/lno.10430, 2017.

Kretz, R.: Calculation and illustration of uncertainty in geochemical analyses. J. Geol. Educ., 33, 40–44, doi:10.5408/0022-1368-33.1.40, 1985.

Kritzberg, E.S., Cole, J.J., Pace, M.L., Granéli, W., Bade, D.L.: Autochthonous versus allochthonous carbon sources of bacteria: Results from whole-lake 13C addition experiments. Limnol. Oceanog., 49, 588-596, doi:10.4319/lo.2004.49.2.0588, 2004.

Ku, H.H.: Notes on the use of propagation of error formulas. J. Res. Nat. Bur. Stand. Sect. C., 70, 263–273, 1966.

Liu, X., Wendt-Potthof, K., Barth, J. A. C., and Friese, K.: Post-depositional alteration of stable isotope signals by preferential degradation of algae-derived organic matter in reservoir sediments. Biogeochemistry, 159, 315–336, https://doi.org/10.1007/s10533-022-00930-y, 2022.

MacKenzie, A.B., Cook, G.T., Barth, J., Gulliver, P., and McDonald, P.: 14C and δ13C characteristics of organic matter and carbonate in saltmarsh sediments from south west Scotland. J. Environ. Monit., 6, 441-447, doi:10.1039/B315766K, 2004.

Mazuecos, I.P., Arístegui, J., Vázquez-Domínguez, E., Ortega-Retuerta, E., Gasol, J.M., and Reche, I.: Temperature control of microbial respiration and growth efficiency in the mesopelagic zone of the South Atlantic and Indian Oceans. Deep-Sea Res. I: Oceanogr. Res. Pap., 95, 131-138, doi:10.1016/j.dsr.2014.10.014 2016.

McDonald, C. P., Saeed, M. N., Robertson, D. M., and Prellwitz, S.: Temperature explains the formation of a metalimnetic oxygen minimum in a deep mesotrophic lake. Inland Waters, 1-10, doi: 10.1080/20442041.2022.2029318, 2022.

Mi, C., Shatwell, T., Ma, J., Wentzky, V. C., Boehrer, B., Xu, Y., and Rinke, K.: The formation of a metalimnetic oxygen minimum exemplifies how ecosystem dynamics shape biogeochemical processes: A modelling study. Water Res., 115701, doi:10.1016/j.watres.2020.115701, 2020.

Nix, J.: Contribution of hypolimnetic water on metalimnetic dissolved oxygen minima in a reservoir. Water Res., 17, 329–332, doi:10.1029/WR017i002p00329, 1981.

Pace, M. L., and Prairie, Y.: Respiration in lakes. In: Respiration in Aquatic Ecosystems, doi: 10.1093/acprof:oso/9780198527084.003.0007, 2005.

Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P., and Guth, P.: Global carbon dioxide emissions from inland waters. Nature, 503, 355-359, doi:10.1038/nature12760, 2013.

Nürnberg, G. K., LaZerte, B. D. and Olding, D. D.: An Artificially induced Planktothrix rubescens surface bloom in a small kettle lake in Southern Ontario compared to blooms world-wide. Lake Reservoir Manag. 19, 307-322, doi: 10.1080/07438140309353941, 2003.

Regnier, P., Friedlingstein,P., Ciais, P., Mackenzie, F.T.,Gruber, N., Janssens, I.A., Laruelle, G.G., Lauerwald, R., Luyssaert, S., Andersson, A.J., Arndt, S., Arnosti, C., Borges, A.V., Dale, A.W., Gallego-Sala, A., Goddéris, Y., Goossens, N., Hartmann, J., Heinze, C., Ilyina, T., Joos, F., LaRowe, D.E., Leifeld, J., Meysman, F.J.R., Munhoven, G., Raymond, P.A., Spahni, R., Suntharalingam, P., and Thullner, M.: Anthropogenic perturbation of the carbon fluxes from land to ocean. Nat. Geosci., doi:10.1038/NGEO1830, 2013.

Rinke, K., Kuehn, B., Bocaniov, S., Wendt-Potthoff, K., Büttner, O., Tittel, J., Schultze, M., Herzsprung, P., Rönicke, H., Rink, K., Rinke, K., Dietze, M., Matthes, M., Paul, L., and Friese, K.: Reservoirs as sentinels of catchments: the Rappbode Reservoir Observatory (Harz Mountains, Germany). Environ. Earth Sci., 69, 523-536, doi:10.1007/s12665-013-2464-2, 2013.

Robarts, R.D. Decomposition is freshwater ecosystems. Journal of the Limnological Society of Southern Africa, 12, 72-89, doi:10.1080/03779688.1986.9639399, 1986.

Scavia, D., and Laird, G. A.: Bacterioplankton in Lake Michigan: Dynamics, controls, and significance to carbon flux. Limnol. Oceanogr., 32, 1017-1033, doi:10.4319/lo.1987.32.5.1017, 1987.

Schindler, D. W., and Gunn, J. M.: Dissolved organic carbon as a controlling variable in lake trout and other Boreal Shield lakes. Boreal Shield watersheds: Lake trout ecosystems in a changing environment. Edited by J.M. Gunn, R.J. Steedman, and R.A. Ryder. Lewis Publishers, Boca Raton, Fla, 133-146, 2004.

Schulte, P., van Geldern, R., Freitag, H., Karim, A., Négrel, P., Petelet-Giraud, E., Probst, J-L., Telmer, K., Veizer, J., and Barth, J.A.C.: Applications of stable water and carbon isotopes in watershed research: weathering, carbon cycling, and water balances. Earth Sci. Rev., 109, 20-31, doi:10.1016/j.earscirev.2011.07.003, 2011.

Shapiro, J.: The cause of a metalimnetic minimum of dissolved oxygen. Limnol. Oceanogr., 5, 216-227, 1960.

Sommer, U., Gliwicz, Z. M., Lampert, W. I., and Duncan, A.: The PEG-model of seasonal succession of planktonic events in fresh waters. Arch. Hydrobiol., 106, 433-471, 1986.

Stiller, M., and Nissenbaum, A.: A stable carbon isotope study of dissolved inorganic carbon in hardwater Lake Kinneret (Sea of Galilee). S. Afr. J. Sci., 95, 166–170, https://hdl.handle.net/10520/AJA00382353_8243, 1999.

Sun, L., Leybourne, M., Rissman, C., and Brikowski, T.: Geochemistry of a large impoundment – part II: Fe and Mn cycling and metal transport. Geochem. Explor. Environ. Anal., 16, 165–177, doi:10.1144/geochem2015-361, 2016.

Thurman, E.M.: Organic geochemistry of natural waters. Martinus Nijhoff / Dr W. Junk Publishers, 1985.

Tittel., J., Hüls, M., and Koschorreck, M.: Terrestrial Vegetation Drives Methane Production in the Sediments of two German Reservoirs. Sci. Rep, 9, https://doi.org/10.1038/s41598-019-52288-1, 2019.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R.G., Ballatore, T. J., Dillon, P., Finlay, K., Fortino, K., Knoll, L. B., Kortelainen, P. L., Kutser, T., Larsen, S., Laurion, I., Leech, D. M., McCallister, S. L., McKnight, D. M., Melack,, J. M., Overholt, E., Porter, J. A., Prairie, Y., Renwick, W. H., Roland, F., Sherman, B. S., Schindler, D. W., Sobek, S., Tremblay, A., Vanni, M. J., Verschoor, A. M., von Wachenfeldt, E., and Weyhenmeyer, G. A.: Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr., 54, 2298–2314, doi:10.4319/lo.2009.54.6_part_2.2298, 2009.

Van Geldern, R., Schulte, P., Mader, M., Baier, A., and Barth, J.A.C.: Spatial and temporal variations of pCO2, dissolved inorganic carbon, and stable isotopes along a temperate karstic watercourse. Hydrol. Process., 29, 3423-3440, doi:10.1002/hyp.10457, 2015.

Wachniew, P.: Isotopic composition of dissolved inorganic carbon in a large polluted river: the Vistula, Poland. Chem. Geol., 233, 293–308, doi:10.1016/j.chemgeo.2006.03.012, 2006.

Weiler, R.R.: Exchange of carbon dioxide between the atmosphere and Lake Ontario. J. Fish. Res. Bd. Can., 31, 329-332, doi:10.1139/f74-053, 1974.

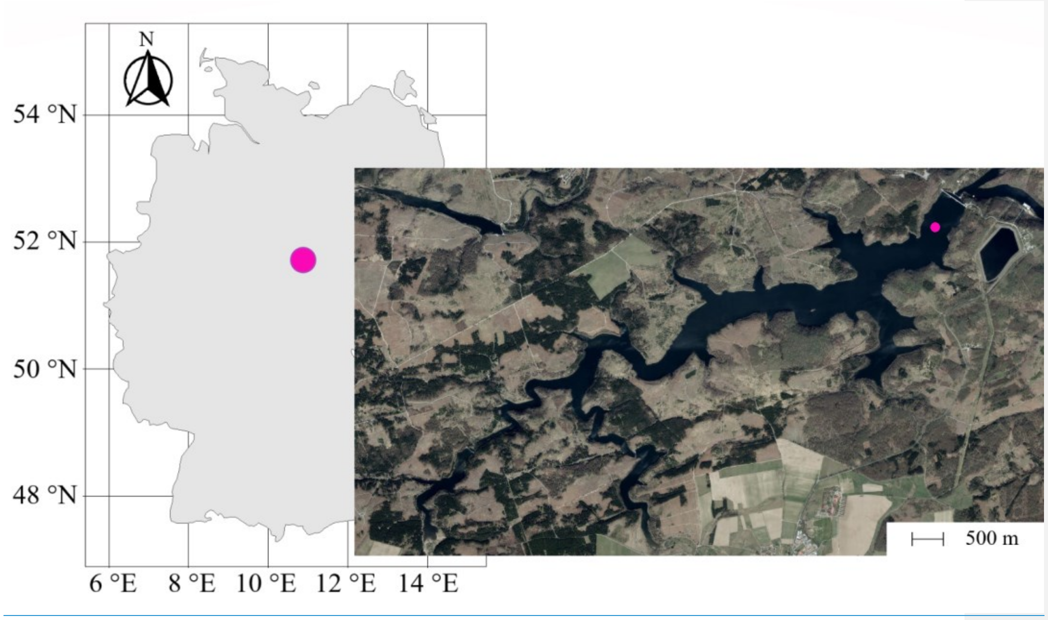
Wentzky, V., Frassl, M.A., Rinke, K., and Boehrer, B.: Metalimnetic oxygen minimum and the presence of Planktothrix rubescens in a low-nutrient drinking water reservoir. Water Res., 148, doi:10.1016/j.watres.2018.10.047, 2019.

Wetzel, R.G.: Limnology. 2nd Edition, Saunders College Publishing, Philadelphia. ISBN: 0-03-057913-9, 1983.

Wetzel, R.G., Rich, P.H., Miller, M.C., and Allen, H.L.: Metabolism of dissolved and particulate detrital carbon in a temperate hard-water lake. Mem. Ist. Ita. Idrobiol., 29, 185-243, 1972.

Willey, J. D., Kieber, R. J., Eyman, M. S. Jr., and Brooks Avery, G.: Rainwater dissolved organic carbon concentrations and global flux. Glob. Biogeochem. Cycles, 14, 139–148, doi:10.1029/1999GB900036, 2000.

Wu, J. L., and Chen, M.: Effects of nitrogen and phosphorus on phytoplankton composition and biomass in 15 subtropical, urban shallow lakes in Wuhan, China. Limnologica, 41, 48–56, doi:10.1016/j.limno.2010.03.003, 2011.


N
54 °N
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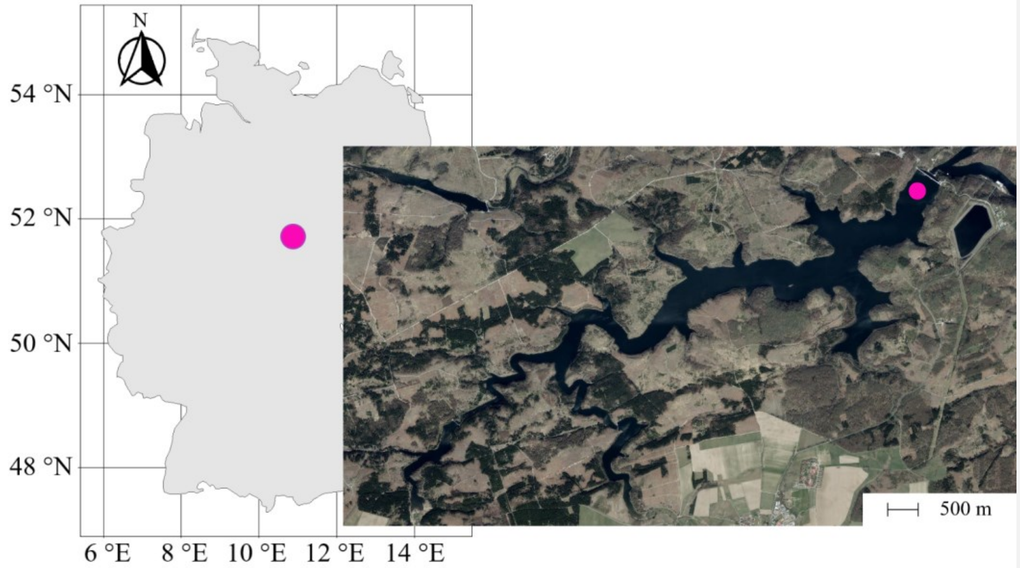


Figure 1 : Position of the Rappbode Reservoir in Germany with the sampling location marked by a pink point in the main reservoir (source: ESRI). 670

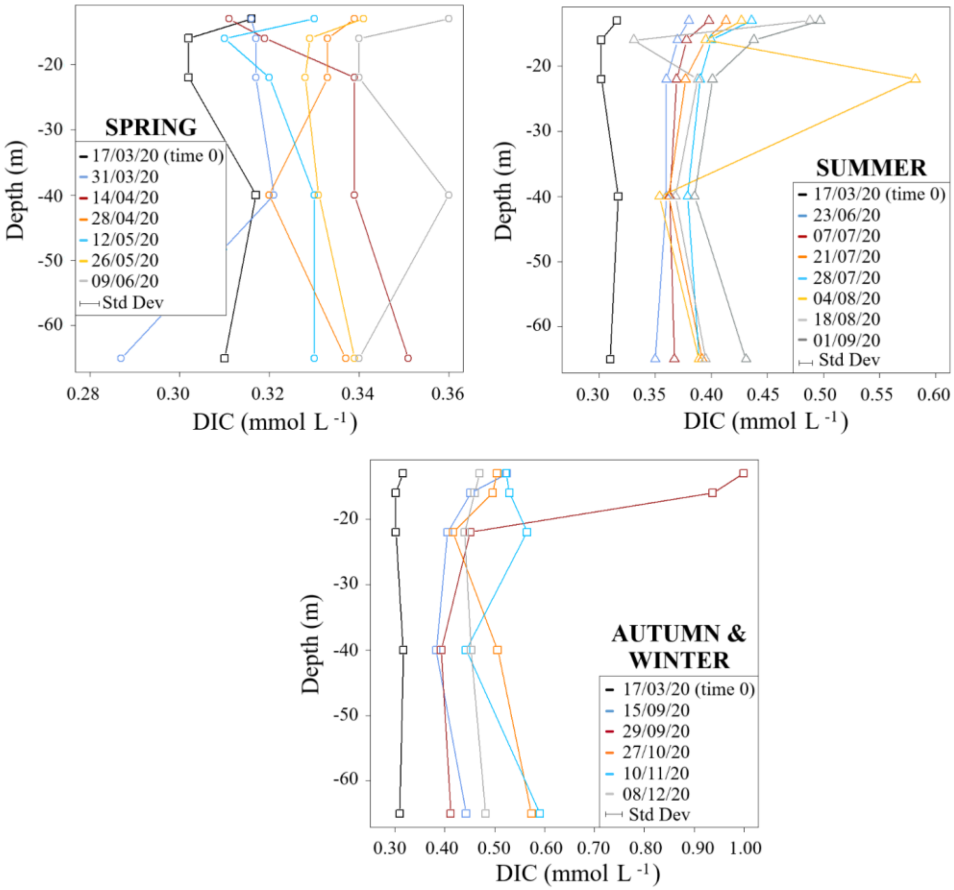


Figure 2 : DIC seasonal concentration profiles. Standard deviations relative to each dataset (± 3%) are reported in the plot below the legend.

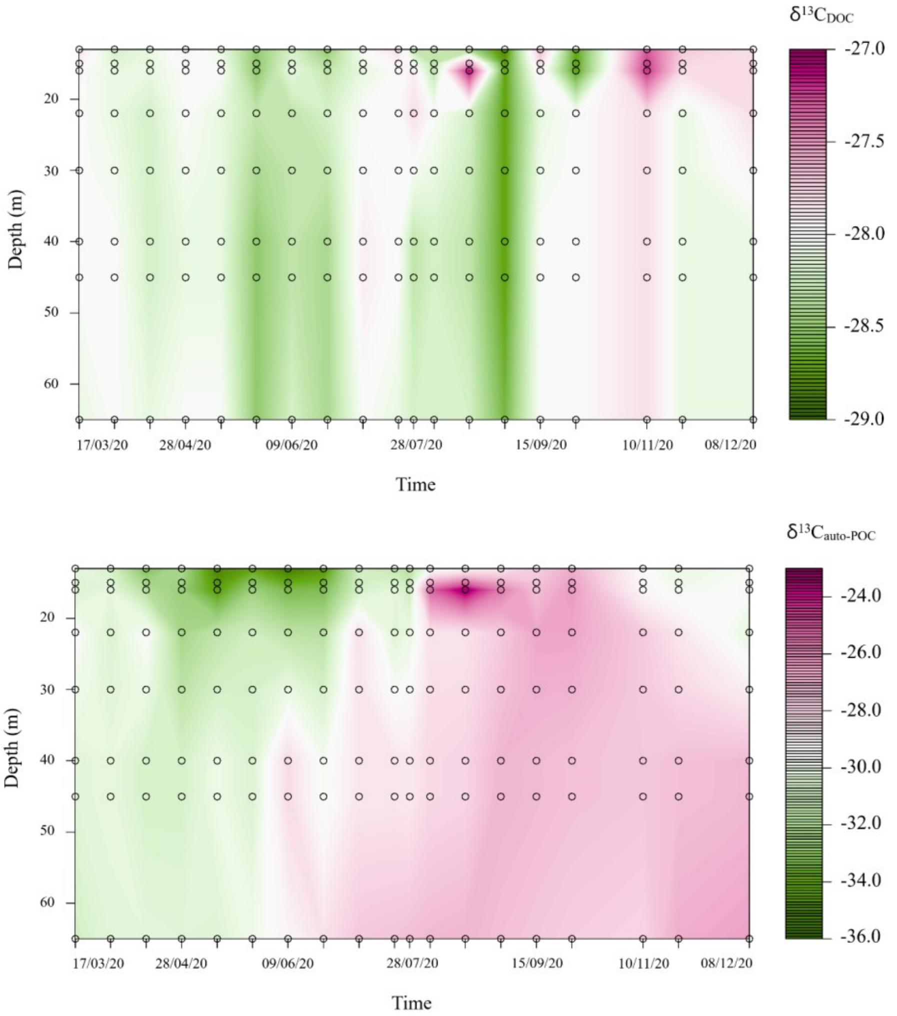
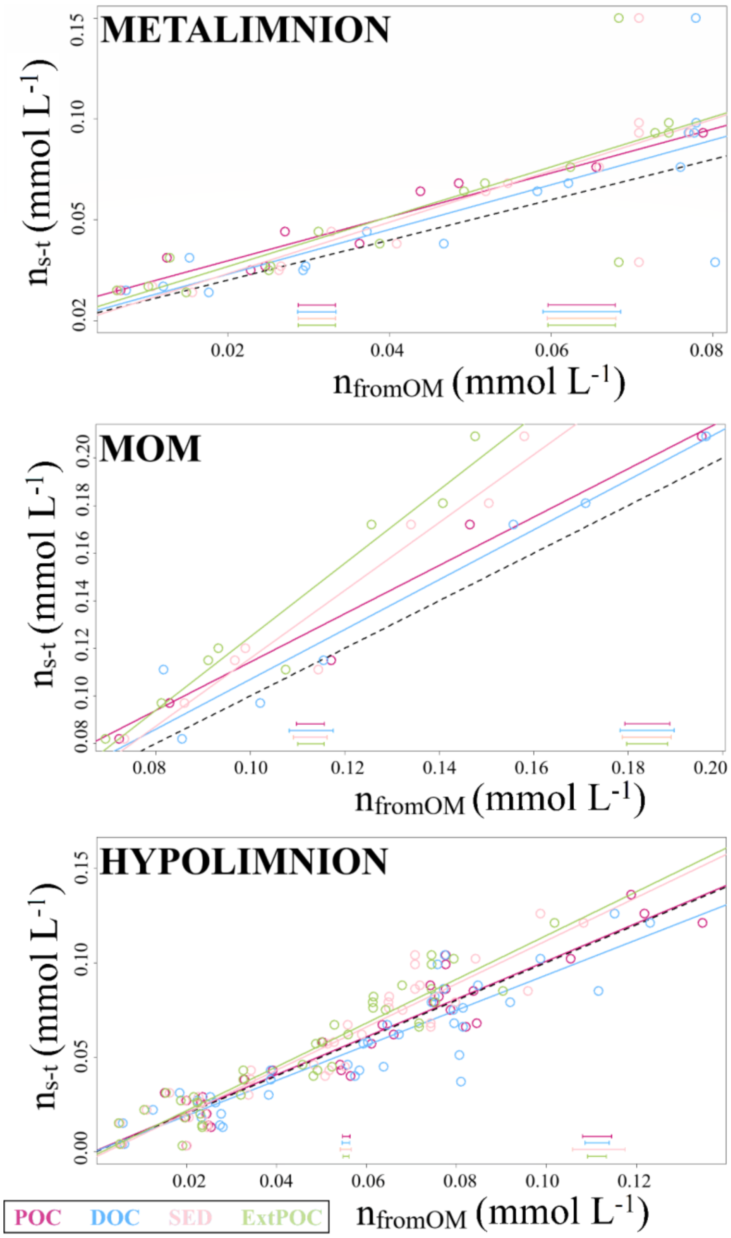


Figure 3 : Carbon stable isotopes variations (‰) of dissolved organic carbon (DOC) and autochthonous particulate organic carbon (auto-POC) during the observation period in the metalimnion and hypolimnion of Rappbode Reservoir.


METALIMNION
$n_{s\text{-}t}$ (mmol L^{-1})
0.02
0.05
0.10
0.15
0.02
0.04
0.06
0.08
n_{fromOM} (mmol L^{-1})
MOM
$n_{s\text{-}t}$ (mmol L^{-1})
0.08
0.10
0.12
0.14
0.16
0.18
0.20
0.08
0.10
0.12
0.14
0.16
0.18
0.20
n_{fromOM} (mmol L^{-1})
HYPOLIMNION
$n_{s\text{-}t}$ (mmol L^{-1})
0.00
0.05
0.10
0.15
0.02
0.04
0.06
0.08
0.10
0.12
n_{fromOM} (mmol L^{-1})
POC DOC SED ExtPOC

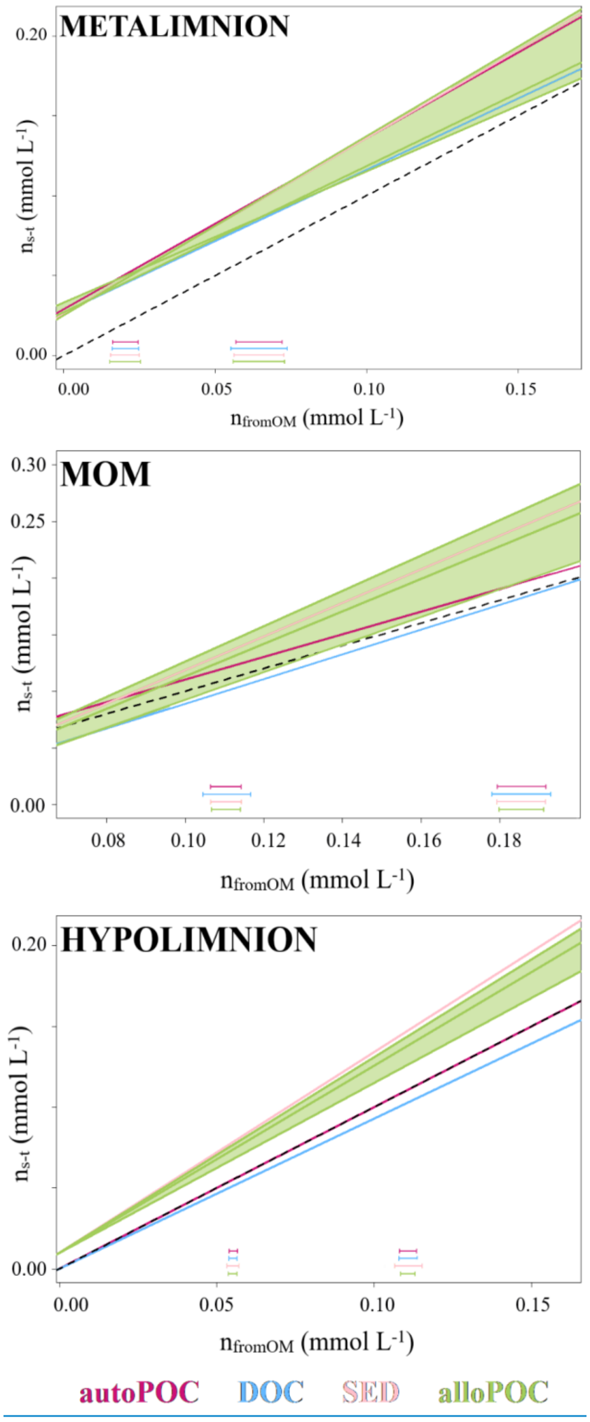

METALIMNION
0.20
0.00
$n_{s\text{-}t}$ (mmol L^{-1})
0.00
0.05
0.10
0.15
n_{fromOM} (mmol L^{-1})
MOM
0.30
0.25
0.00
$n_{s\text{-}t}$ (mmol L^{-1})
0.08
0.10
0.12
0.14
0.16
0.18
n_{fromOM} (mmol L^{-1})
HYPOLIMNION
0.20
0.00
$n_{s\text{-}t}$ (mmol L^{-1})
0.00
0.05
0.10
0.15
n_{fromOM} (mmol L^{-1})
autoPOC
DOC
SED
alloPOC

Figure ~~3~~4 : Molar gain by concentration from time 0 (n_{s-t}) and as calculated by mass balance with carbon stable isotopes (n_{fromOM}) in the metalimnion, MOM and hypolimnion of the Rappbode Reservoir. Datasets are reported in different colours according to the considered OM. Green fields represent the variation of allo-POC. Standard variations for each OM are reported within the plot.

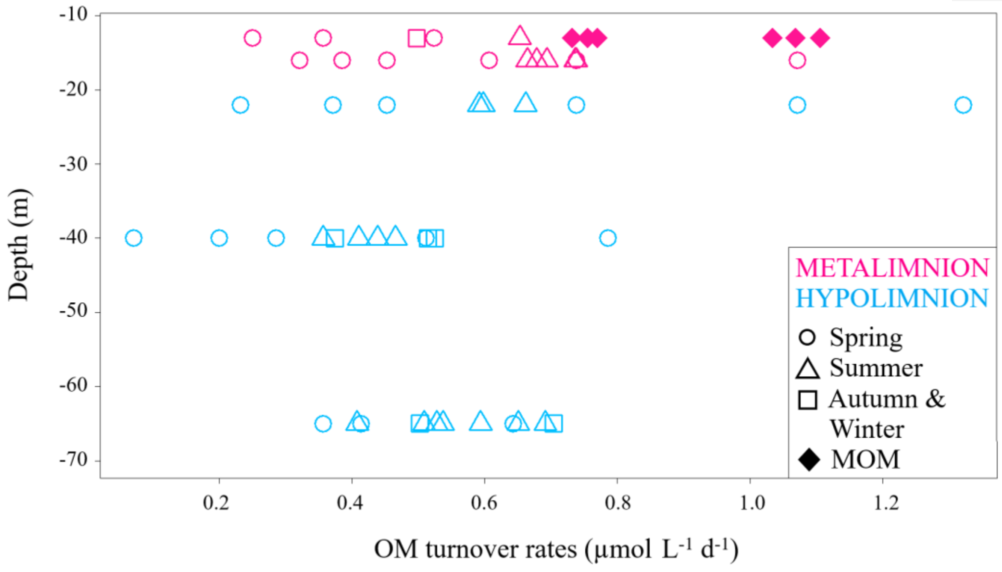


Figure ~~5~~4 : DIC production rates at specific depths of the hypolimnion and metalimnion during the studied time period, marked with different symbols according to sampling season. MOM samples belong to summertime and are displayed as diamond shapes for clarity.

OM input →	Auto-POC	DOC	SED	Allo-~~Ext~~POC
Metalimnion	y = 1.107~~2~~x + 0.03~~1~~ $R^2 = 0.95$	y = 0.892~~1.15~~x + 0.0~~0~~3 $R^2 = 0.85$	y = 1.~~35x~~ 10x +- 0.~~00~~03 R^2 = 0.94~~88~~	y = (0.82 to 1.21)~~1.34~~x + 0.03~~0~~ R^2 = 0.~~88~~92
MOM	y = 1.01x + 0.01 $R^2 = 0.95$	y = 1.09x - 0.02 $R^2 = 0.94$	y = 1.48~~3~~x - 0.03 $R^2 = 0.943$	y = (1.22 to 1.56)4x - 0.03 $R^2 = 0.94$
Hypolimnion	y = 1.00x + 0.00 $R^2 = 0.91$	y = 0.93x + 0.00 $R^2 = 0.82$	y = 1.244~~1~~x +- 0.01~~0~~ R^2 = 0.90~~88~~	y = (1.05 to 1.21)~~16~~x +- 0.01~~0~~ R^2 = 0.~~89~~90

Table 1 : Equations of the regression lines for autochthonous particulate organic carbon (auto-POC), dissolved organic carbon (DOC), sedimentary material (SED), and allochthonous particulate organic carbon (allo-~~Ext~~POC) in the metalimnion, MOM and hypolimnion of the Rappbode Reservoir. The coefficient of determination (R^2) is reported below each equation. All p-values < 0.001.

Formatted Table