Post-depositional alteration of stable isotope signals by preferential degradation of algae-derived organic matter in reservoir sediments

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Abstract Post-depositional degradation of organic matter (OM) in freshwater sediments is crucial for driving the biogeochemical dynamics and influencing the carbon burial. This process also often causes diagenetic alteration on paleoenvironmental proxies. Yet, mechanisms behind degradation of sedimentary OM and depth-related variations in stable isotope ratios can so far only be explained in part. Degradation of sedimentary OM in two drinking water reservoirs with contrasting eutrophic and mesotrophic states and different catchment land use (agriculture versus forestry) was studied. A 4-step procedure was used to chemically separate sedimentary OM in terms of biochemical composition. Here we presented depth profiles of biochemical composition of sedimentary OM that helped to quantify preferential degradation of aquatic proteins and carbohydrates and the following removal of aquatic lipids. Sediment in the eutrophic reservoir, which reflected a larger contribution of algal-derived OM than the mesotrophic reservoir with a forest dominated catchment, was therefore subject to more intensive degradation of sedimentary OM along with δ13C and δ15N alterations. In addition, changes in the relative proportions of biochemical components in sedimentary OM had more pronounced impact on δ15N values relative to δ13C. Our findings suggest that the lability of algae-derived OM leads to uncertainties for the estimation of carbon burial in water bodies and obscures paleo-limnological information derived from isotopic proxies. Post-depositional modifications are more pronounced in eutrophic freshwaters that accumulated more readily degradable OM of algal origin in their sediments. Recognition of these modifications will help constrain carbon burial rates of productive lakes and reservoirs and assess the role of reservoirs in carbon cycling.

Keywords Carbon burial · Paleolimnology · Preferential degradation · Sedimentary organic matter · Stable isotopes
Introduction

Even though freshwaters have a much smaller area compared to the oceans, they accumulate large quantities of carbon in their water columns and sediments (Tranvik et al. 2009). Estimates for reservoirs alone account for an annual global sequestration of about 0.06 Pg organic carbon (OC) (Mendonça et al. 2017). Such high OC burial rates in reservoir sediments are attributed to high production rates per unit area, efficient sediment retainment and large amount of terrestrial organic matter (OM) inputs. The latter results from high ratios of catchment area to surface area of reservoirs and short OM transport distances (Hayes et al. 2017). Moreover, OM in reservoirs undergoes intensive mineralization, which turns most reservoirs into strong methane emitters (Beaulieu et al. 2020; Deemer et al. 2016; Tittel et al. 2019). A recent study on methane ebullition has predicted an increasing release of methane from reservoirs in response to changes in land use and climate (Aben et al. 2017).

The active cycling of carbon in reservoirs closely relates to degradation dynamics of OM in sediments. Organic components with high bioavailability are preferentially decomposed or consumed by bacteria in lakes and reservoirs (Cowie and Hedges 1994). This preference causes discrepancies between sedimentary OC accumulation and long-term OC burial, which could give rise to underestimates of OC burial rate in lakes by 10% (Anderson et al. 2013). These discrepancies could be more conspicuous in reservoirs in response to changes in land use and climate (Anderson et al. 2013). These features are conventionally used as geochemical proxies to trace OM sources and to reconstruct paleolimnological environments (Meyers and Eadie 1993). For example, stable carbon and nitrogen isotope ratios (expressed as δ^{13}C and δ^{15}N) in conjunction with molar carbon to nitrogen ratio (C/N) were used to outline allochthonous and autochthonous origins of OM in sediments (Das et al. 2013; Meyers and Eadie 2003). Similar approaches were adopted to distinguish vegetation sources (e.g., C_3 versus C_4 plants) in a catchment (Meyers and Lallicher-Vergès 1999). Sedimentary δ^{13}C and δ^{15}N also recorded lake eutrophication with a negative down-core excursion of ~2‰ for δ^{13}C and ~3‰ for δ^{15}N in subtropical lakes (Braig et al. 2013; Torres et al. 2012). Post-depositional processes may hamper interpretations of down-core trends of these biogeochemical proxies. Thus, biochemical investigations of degradation patterns of sedimentary OM in freshwater sediments are crucial for more reliable estimates of OC burial and reconstructions of paleoenvironments.

Factors that determine regimes and paces of sedimentary OM degradation include geography, hydrology, morphology and catchment land use of lakes and reservoirs (Berberich et al. 2020; Darrow et al. 2017). All these factors influence the primary production and trophic states in the water column and subsequently degradability of allochthonous OM. Contribution from aquatic or terrestrial sources, which largely determines the degree of aliphaticity and aromaticity of OM (Gontijo et al. 2021), further influences the degradability of sedimentary OM. Next to its sources, conditions that may restrict the degradation of OM in sediments include thermodynamic characteristics of OM (Fabiano et al. 1995; Tittel et al. 2019), microbial activities during deposition (Boetius and Lochte 1994), redox potential (Nierop et al. 2017) and temperature. In addition, physical protection and post-depositional transformation of OM (e.g., humification and condensation-polymerization) may alter the composition and degradability of the remaining OM as well (Gupta et al. 2007; Middelburg 2018). Such alterations are mostly connected to the preferential degradation of labile organic components.

Degradation of sedimentary OM is either studied to determine magnitudes of sedimentary carbon sinks or to trace processes of OM oxidization, transformation and preservation (Bastviken et al. 2003). Other purposes include evaluations of diagenetic impacts and isotope alterations for the interpretations of paleo-limnological proxies (Zonneveld et al. 2010). For instance, information about depth profiles of OM composition and associated degradation rates of organic components can help to elucidate OM processing during early diagenesis. Usually, OM composition is examined by combinations of chemical extractions to address specific target organic components. Most existing methods cannot entirely identify all organic components in sediments, and proportions of characterizable OM decrease with depth. Moreover, impacts of post-depositional
OM degradation on OC burial and isotope proxies remain under debate (Anderson et al. 2013; Herczeg 1988; Hodell and Schelske 1998). Associated uncertainties most frequently arise from different burial environments and their redox conditions together with diverse responses between C and N isotopes to degradation. So far, most studies on degradation of OM were carried out in natural lakes and coastal regions, while little is known about sedimentary OM processes in reservoirs or human-impacted lakes. The latter host special environments with high sedimentation and OC burial rates and often low oxygen concentration in their sediments. Overall, mechanisms of OM degradations in freshwaters show strong regional disparities and have not been well established in eutrophic freshwaters.

Here, we present observations of OM processing in two adjacent freshwater reservoirs with contrasting trophic states and aim to clarify diagenetic fates of OM and related modifications of isotopic signals. The objectives of our study were

(1) to gain a biochemical insight into post-depositional degradation pathways of OM in recently deposited sediments,

(2) to investigate down-core variations of sedimentary stable isotope ratios that may relate to early diagenesis, and

(3) to outline impacts of catchment land use on the degradation of OM in sediments.

The findings of this study are useful to elucidate burial of OC and can provide more evidence for diagenesis-related modifications of sedimentary stable isotopes. These new results may be particularly important for more accurately estimating contemporary OC burial rates and reconstructing paleo-limnological environments of productive and eutrophic lakes or reservoirs.

Materials and methods

Site description

The study site, Hassel and Rappbode pre-dams, are located in the eastern Harz Mountains (Fig. 1), as part of the largest drinking water reservoir (Rappbode Reservoir System) in Germany. Rappbode and Hassel pre-dams are impoundments reconstructed from two tributaries in front of the main reservoir in the 1960s. Pre-dams serve as sedimentation basins for the reduction of particle and nutrient loads (Friese et al. 2014), and their deep water zones are lake-like with surface outflows to the main dam. However, they have usually shorter water retention time and greater water surface to catchment area ratio than natural lakes. Hassel pre-dam has a surface area of 0.26 km² and an impounding capacity of $1.64 \times 10^6$ m³ with a residence time around 65 days (Dadi et al. 2016). The deepest site of the pre-dam is 14 m, while the average depth is 5.0 m. Rappbode pre-dam is adjacent to Hassel pre-dam and morphologically similar to Hassel pre-dam in terms of surface area (0.26 km²), water impounding capacity ($1.66 \times 10^6$ m³), mean and maximum depths (5.7 m and 17.0 m, respectively) and catchment area (47.6 km²).

The sub-catchment of Hassel pre-dam covers 44.6 km² with almost equal share of forest, cropped land and grassland area. Farming activities and fertilization in the catchment declined since the re-union of Germany in 1990, which was followed by a dramatic decrease of nutrient load in reservoirs (Wentzky et al. 2018). The catchment of Rappbode pre-dam consists of 72% of forest, 22% grassland and almost no agricultural land (Wendt-Potthoff et al. 2014). As part of the Harz tourism area, the land cover of the catchment is well preserved and undergoes no major changes since the construction of pre-dams. Differences in the coverage of agriculture lands between Rappbode and Hassel pre-dam catchments lead to contrasting trophic states in these two pre-dams and can be preserved in sediments accumulated over past few decades (Kurt et al. 2014).

Sediment cores were taken from the deep and shallow sites of pre-dams (Fig. S1), which reflected largely the riverine and lake-like depositional conditions, respectively, for particulate OM. In Rappbode pre-dam, a shallow site (51.70 °N, 10.79 °E, 4 m in water depth) was located near the riverine inflow, and a deep site (51.71 °N, 10.80 °E, 14 m in water depth) was close to the main dam (Fig. 1). Similarly, the shallow (51.70 °N, 10.83 °E) and deep sampling sites (51.71 °N, 10.83 °E) in Hassel pre-dam have the same water depths (4 m and 14 m, respectively) and enable systematic comparisons with Rappbode pre-dam (Fig. 1). The hypolimnia at both deep sites become anoxic due to stratification during the summer (June
High turbidity layer is found in the epilimnion of Hassel pre-dam, but it occurs in the hypolimnion of Rappbode pre-dam (Friese et al. 2014). The physicochemical properties of these two pre-dams are listed in Table 1. Rappbode pre-dam is mesotrophic and has a relatively higher sedimentation rate and terrestrial carbon input than Hassel pre-dam. Hassel pre-dam is eutrophic with a higher nutrient load and thus higher primary production compared to Rappbode pre-dam.

Sediments and suspended particulate organic matter sampling

Sediments were sampled with a modified Kajak gravity corer (UWITEC, Austria) fixed with a polyvinyl chloride (PVC) cylindrical tube (9 cm in diameter, 60 cm in length) in April, 2011. Sediment cores were protected with a tight cover and kept secured upright position during transportation. In the laboratory, sediment columns were then cut into 2 cm slices and enclosed in pre-weighted polypropene plastic vials for freeze-drying. Sediment grain size was sorted as clay, fine silt, medium silt, coarse silt and sand (i.e., grain size of <2, 2–10, 10–20, 20–63, > 63 µm, Table S1 and Fig. S1 in Supporting Information). Large pieces of rock and plant detritus (> 2 cm in length) were picked out manually according to the sediment preparation protocol suggested by the International Atomic Energy Agency (Smidis et al. 2003), before dry sediments were milled with agate mortar. Well-ground sediments were then weighed and stored for subsequent measurements.

Suspended particulate organic matter (POM) in the water column was sampled to obtain general information about algae in pre-dams. Duplicate surface water samples were collected (20 L for each sample) at the deep sites of Hassel and Rappbode pre-dams. In the laboratory, suspended material was separated from the bulk water samples by ultrafiltration. Briefly, a volume of 19 L water sample was passed through a 0.45 µm ultrafiltration cassette (C613, Pellicon), and
then 1 L residual concentrated water was centrifuged (10,000 rpm for 15 min, Beckman Coulter J2-MC High Speed Centrifuge, Minnesota, United States of America). The centrifugal precipitate was dried at 45 °C and milled for POM characterization. Previous analyses (Friese et al. 2014; Barth et al. 2017) on the suspended material collected from the same sampling sites (surface water at the deep site) indicated that the POM consisted mainly of cyanobacteria in Rappbode pre-dam and by diatoms in Hassel pre-dam.

Chemical fractionation of OM in sediments

A newly developed four-step chemical fractionation, which treated sediments subsequently with hot water, hydrochloric acid (HCl), hydrogen peroxide (H₂O₂) and disodium peroxodisulfate (Na₂S₂O₈), was applied to group the bulk sedimentary OM into four portions (Liu et al. 2020). In brief, the powdered sediments (3 g) were first treated with hot water (80 °C) for 18 to 24 h as a mild extraction. Resulting hot water extracted residues (2 g) were successively hydrolyzed with 6 M HCl at 80 °C for about 20 h. One gram of the remaining solids was further oxidized repeatedly by H₂O₂ (10%) at a temperature of 50 °C until effervescence ceased. In the end, half a gram of the recalcitrant residue was exposed to Na₂S₂O₈ which was buffered with sodium bicarbonate (NaHCO₃) overnight (80 °C). The retained bicarbonate in suspension was neutralized by 1 M HCl. Solid residues from each chemical extraction step were collected and dried for further characterization. The chemical fractionation procedure proceeded in triplicate for one or two depths as representative shallow and deep sediments.
of each sediment core, to evaluate the inherent variability of ground sediments.

To obtain a full depth profile of OM composition, sediments from each 2 cm slice were subsampled and treated using the above sequential fractionation method, and obtained sedimentary OM fractions were determined for elemental and stable isotope compositions. Our previous work demonstrated that hot water extracts only a small fraction of microbial and soluble proteins and polysaccharides. Furthermore, HCl extracts the remaining majority of proteins, carbohydrates and carboxylic lipids; H$_2$O$_2$ oxidizes lignins, lipids and some complex proteins; and Na$_2$S$_2$O$_8$ removes almost the remaining lipids (Liu et al. 2020). Down-core variations in the composition of sedimentary OM fractions thus can be ascribed to the diagenesis of specific organic components.

Stable isotope ratio analyses

Total organic carbon (TOC), total nitrogen (TN), stable carbon and nitrogen isotope compositions of untreated bulk sediments and chemical extraction residues were measured by isotope ratio mass spectrometry (IRMS, DELTA V advantage, Thermo Fisher Scientific, Bremen, Germany) that was coupled to an elemental analyzer (EA, Flash 2000, Thermo Fisher Scientific, Bremen, Germany). Five milligrams of untreated bulk sediments as well as hot water- and HCl-treated sediment residues were selected for stable isotope ratio measurements. Sample weights were increased to 20 mg for H$_2$O$_2$- and Na$_2$S$_2$O$_8$-treated sediment residues in order to increase peak signals for isotope analyses, especially for $^{15}$N. Homogenized sediment residues were combusted into CO$_2$, CO, NOx, N$_2$, H$_2$, SO$_2$. From this mixture CO$_2$ and N$_2$ were first oxidized and reduced then chromatographically separated and then sequentially submitted to the IRMS for stable isotope determination. Elemental compositions were measured as mass fraction (wt%) and converted to absolute C and N weights in one gram of dry sediments (mg g$^{-1}$). Carbon to nitrogen ratios (C/N) are given in molar ratios in this work. Stable carbon and nitrogen isotope ratios ($\delta^{13}$C, $\delta^{15}$N) are presented in parts per mil (‰) with reference to the Vienna PeeDee Belemnite (V-PDB) and AIR standards, respectively (Coplen et al. 2006; Kayler et al. 2011). The 1-$\sigma$ precision of measurement was $\pm 0.1$‰ for $\delta^{13}$C and $\pm 0.2$‰ for $\delta^{15}$N based on repeat analyses ($n=6$) of well mixed bulk field samples. More analytical details are available in Liu et al. (2020).

Two-source mixing model for sedimentary organic matter

Atomic C/N ratio of sediments is the proxy for the relative contribution of aquatic and terrestrial OM to sediments (Das et al. 2013). Full depth profiles of atomic C/N ratios were obtained from analytical results of sedimentary C and N contents. To evaluate the relative composition of land- and algal-derived OM in sediments, a two-source (aquatic and terrestrial) mixing model based on the following equation was employed (Guillemette et al. 2017),

$$\frac{C}{N}_{\text{sediment}} = (1 - f)\frac{C}{N}_{\text{terrestrial}} + f\frac{C}{N}_{\text{aquatic}}$$

where f is the relative proportion of aquatic OM in sediments; $\frac{C}{N}_{\text{sediment}}$, $\frac{C}{N}_{\text{terrestrial}}$, and $\frac{C}{N}_{\text{aquatic}}$ are the molar C/N ratio of the bulk sediments, the soil from the catchment and algae in the euphotic zone of the reservoir, respectively. The mean soil C/N ratios in Rappbode and Hassel catchments are 15.4 ± 2.2 (n = 3) and 13.1 ± 0.9 (n = 3), respectively (Schönfeldt 2013). Due to the overwhelming dominance of phytoplankton in suspended POM (Friese et al. 2014), C/N values of suspended POM in surface water at the deep sites of both reservoirs were used as $\frac{C}{N}_{\text{aquatic}}$ in the mixing model.

Chemical composition analyses using $^{13}$C nuclear magnetic resonance

Preliminary isotopic measurements indicated the discrepancy of $\delta^{13}$C and $\delta^{15}$N shifts between treatments with HCl and H$_2$O$_2$ among different sampling sites. This discrepancy was pronounced for deep sediments below 10 cm. Therefore, both HCl and H$_2$O$_2$ resistant residues of relatively deep sediments (14–16 cm) were analyzed by $^{13}$C nuclear magnetic resonance (NMR) for chemical structure in order to interpret the site-specific shifts in $\delta^{13}$C and $\delta^{15}$N after H$_2$O$_2$ oxidation. These analyses were performed on a Bruker Avance 300 NMR spectrometer (Bruker Biospin, Bremen, Germany), coupled with Cross Polarization/Magic Angle Spinning (CP/MAS). The spectrometer was operated at a $^{13}$C frequency of 75.47 MHz. The
proton 90° pulse was set to 3.3 µs, and the decoupling strength during acquisition was 69 kHz. The $^{13}$C NMR spectra were acquired applying a spinning rate of 5 kHz with a 4 mm diameter cylindrical zirconia rotor, a recycle delay of 2 s and a contact time of 2 ms. All spectra were processed with a Lorentzian line broadening of 1 Hz.

Spectra of $^{13}$C NMR analyses were analyzed using TopSpin 3.5 (Bruker, Biospin). Chemical shifts in the spectra were externally referred to the glycine resonance at 176.03 ppm and recorded from −100 to 300 ppm after linear baseline correction. Integrations of $^{13}$C NMR spectra were accomplished by grouping the chemical shift into regions as alkyl C (0–45 ppm), N-alkyl-methoxy C (45–60 ppm), O/O$_2$-alkyl C and acetals (60–100 ppm), aromatic C (100–145 ppm), O-aromatic C with phenols (145–165 ppm), esters, carboxyl or carbonyl C (165–215 ppm) (Rodríguez-Murillo et al. 2011). To better evaluate the terrestrial and aquatic nature of sedimentary OM, organic compounds were assessed by aliphaticity and aromaticity (Wehrl and Wirthlin 1976), which were based on the H/C ratio, to infer the ability of carbon to synthesize long chain or hexagonal rings, respectively (Ryan and Ledda 1997). The aliphaticity and aromaticity of sedimentary OM here were taken as the areas of $^{13}$C NMR spectroscopic integration between 0 and 100 ppm and 100 to 165 ppm, respectively, with reference to dos Santos et al. (2010).

Statistical analysis

Mean values and standard deviations of elemental and stable isotope compositions were calculated for sediment samples with replicates. Magnitudes of organic components removed progressively by chemical fractionation were quantified from differences of TOC or TN contents of sediment residues between two successive fractionation steps. Down-core variations in TOC, TN, $\delta^{13}$C and $\delta^{15}$N values of untreated bulk sediments were simulated by generalized additive models (GAM) with the R package “mgcv”. Assuming the accumulation of sediments was a time series, magnitudes of down-core trend in $\delta^{13}$C and $\delta^{15}$N were determined by the Sen’s slope of modified Mann–Kendall trend test. Uncertainty propagation for the two-source mixing mode was accomplished with the R package “propagate”. Geochemical proxies (elemental compositions and stable isotope ratios) were compared between deep and shallow sites within the same pre-dam and between two pre-dams by unpaired Student’s $t$ test. All statistical analyses were conducted under R computational environment in R version 3.4.3 (R Core 2013). Paired Student’s $t$-test was applied for comparisons of stable isotope ratios between two successive fractionation steps. The significance level ($p$) of all the statistical analyses was set at 0.05.

Results

Elemental and isotope compositions of bulk sediments

Suspended particulate organic matter

Suspended matter in Rappbode pre-dam contained on average 191 mg g$^{-1}$ of TOC and 25 mg g$^{-1}$ of TN. Both TOC and TN contents of suspended matter were almost double in Hassel pre-dam with 335 and 45 mg g$^{-1}$, respectively. Suspended matter in Rappbode pre-dam was depleted in $\delta^{13}$C and $\delta^{15}$N relative to Hassel pre-dam, with a mean $\delta^{13}$C value of −31.5‰ and a mean $\delta^{15}$N value of +4.2‰. In contrast, $\delta^{13}$C and $\delta^{15}$N values of suspended matter in Hassel pre-dam were on average −30.4 ‰ and +5.5‰.

Depth profiles of carbon and nitrogen contents

At the deep site of Rappbode pre-dam, the sedimentary TOC content decreased from 86.9 to 61.3 mg g$^{-1}$ (Fig. 2). In comparison, TOC contents at the deep site of Hassel pre-dam ranged from 106.9 mg g$^{-1}$ in surface sediments to 56.6 mg g$^{-1}$ in bottom sediments (Fig. 2). At the shallow site of Rappbode pre-dam, the TOC content was 75.5 mg g$^{-1}$ in surface sediments and stabilized near 60.0 mg g$^{-1}$ below (Fig. 2). The TOC profile at the shallow site of Hassel pre-dam was less variable, with a change from ~63 to ~56 mg g$^{-1}$ over 10 cm depth from the sediment surface (Fig. 2). Overall, sediments at the shallow site of Rappbode pre-dam were more abundant in OC relative to those of Hassel pre-dam ($t = 2.5, p < 0.05$, Student’s $t$ test).

Depth profiles of sedimentary TN content in Rappbode and Hassel pre-dams were similar to those of sedimentary TOC (panels in the two leftmost columns, Fig. 2). At the deep sites, TN contents
decreased downward from 8.9 to 6.0 mg g$^{-1}$ for Rappbode and from 12.4 to 6.3 mg g$^{-1}$ for Hassel sediments (Fig. 2). However, the downward decreases of TN contents in sediment cores at both shallow sites declined to less than 1 mg g$^{-1}$ (6.5 to 5.3 mg g$^{-1}$ for Rappbode pre-dam and 6.9 to 5.7 mg g$^{-1}$ for Hassel pre-dam (Fig. 2). In addition, the Student’s $t$ tests suggested that sediments in both deep and shallow sites of Rappbode pre-dam contained consistently less nitrogen than sediments in Hassel pre-dam ($t = -2.4$, $p < 0.05$ for the deep sites and $t = -3.1$, $p < 0.01$ for the shallow sites).

**Depth profiles of the stable carbon and nitrogen isotope ratios**

Sedimentary $\delta^{13}C$ at the deep site of Rappbode pre-dam showed an increasing trend with respect to the sediment depth ($p < 0.005$, Sen’s slope $= 0.33$, modified Mann–Kendall trend test). It increased from...

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**Fig. 2** Vertical trends of elemental and stable isotope compositions in sediment cores. Black lines are nonlinear correlations that predicted by generalized additive models. Blue shading represents the confidence interval for the given parameters of the predicted nonlinear correlation.
−31.1 to −27.6‰ in the upper 18 cm and remained almost unchanged below this depth (Fig. 2). This trend was different in Hassel pre-dam where the δ13C values at the deep site increased by 3.7‰ in the top to 10 cm sediments (from −31.3 to −27.6‰) and then stabilized. Below 16 cm, δ13C values significantly decreased again from −27.2 to −29.3‰. Also, δ13C value-depth profiles at the shallow sites of these two pre-dams exhibited divergent down-core trends, with a Sen’s slope of 0.05 versus 0.16 (Rappbode versus Hassel) according to the modified Mann–Kendall trend analysis (both \( p < 0.005 \)). The δ13C value was rather invariable in the sediment core at the shallow site of Rappbode pre-dam, while it increased from −29.4 at 10 cm to −28.4‰ to the bottom of the core at the shallow site of Hassel pre-dam (Fig. 2).

A downward enrichment of 15N was observed in sediments at the deep site of Rappbode pre-dam \(( p < 0.0001 \), Sen’s slope = 0.27, modified Mann–Kendall trend test). Sedimentary δ15N increased by 2.6‰ (+2.9 to +5.5‰) over the top 22 cm and remained unchanged below this depth. In contrast, sediments at the deep site of Hassel pre-dam became enriched in 15N. The δ15N value showed an increase from +4.5‰ in the top part of the core to +6.8‰ at 10 cm depth and was followed by a moderate fluctuation from 18 cm to the bottom (Fig. 2). At Rappbode shallow site, sedimentary δ13N exhibited higher depth variabilities when compared to δ13C (Sen’s slope of modified Mann–Kendall trend test: 0.09 versus 0.05, both \( p < 0.005 \)). In addition, based on Student’s t tests on the sedimentary δ15N values for these two shallow sites, sediments of Hassel pre-dam were significantly more enriched in 15N when compared to sediments of Rappbode pre-dam \( ( t = −12.0, p < 0.0001 ) \).

**Compositions of aquatic versus terrestrial organic matter in sediments**

C/N ratios of suspended OM were 9.0±0.1 and 8.7±0.6 for Rappbode and Hassel pre-dams, respectively. These values are lower than those of sedimentary OM (Fig. 3). Overall, sediments in Rappbode pre-dam had larger C/N values than sediments in Hassel pre-dam (Fig. 3). This was also evident by statistical differences in C/N ratios between two deep sites or between two shallow sites (Student’s t test, \( t = 5.0, p < 0.001 \) and \( t = 15.2, p < 0.0001 \) for the deep and shallow sites, respectively).

Sedimentary C/N ratios of the two deep sites underwent disparate down-core modifications. At the deep site of Rappbode pre-dam, sedimentary C/N ratios were almost constant with a minor decrease in depth intervals of 4 to 12 cm and an abrupt increase to about 12 for the bottom sediments (Fig. 3). However, the C/N ratio of sediments at Hassel deep site decreased in the top 6 cm and was followed by a strong increase between 6 and 14 cm below the sediment surface (Fig. 3). Among all sampling sites, the highest C/N ratio was found at the shallow site of Rappbode pre-dam and ranged between 12.7 and 13.5 with no clear down-core trends (Sen’s slope \( \approx 0, p > 0.5 \), modified Mann–Kendall trend test). The C/N ratio-depth profile of sediments at the shallow site of Hassel pre-dam fell between the depth profiles of these two deep sites. The average C/N ratio was 10.5 in the upper 10 cm and increased to 11.2 below 10 cm.

With these C/N ratio-depth profiles, the relative contribution of terrestrial sources in sedimentary OM was then determined by the mixing model. At the deep site of Rappbode pre-dam, sedimentary OM of algal origin consistently prevailed over that with
land-plant origin throughout the core, while sedimentary OM at the shallow site was dominated by terrestrial OM (Table 2). At both deep and shallow sites of Hassel pre-dam, aquatic OM made up a large share of sedimentary OM in the upper 10 cm. Relative proportions of aquatic OM in sediments increased from the core-top to the subsurface (8 and 5 cm for the deep and shallow site, respectively, Table 2). However, below this depth, this proportion decreased abruptly, in particular at the deep site, with a drop from 80 to 60% (Table 2).

Chemical fractions of sedimentary organic matter

**Depth profiles of biochemical composition**

The sequential fractionation procedure defined four OM fractions (hot water extractable, HCl hydrolysable, H$_2$O$_2$ oxidizable and Na$_2$S$_2$O$_8$ oxidizable OM), which consisted of more than 96% of TOC and TN in sediments. On average less than 2 mg g$^{-1}$ TOC and almost no nitrogen was left in the residual sediments after the entire sequential fractionation (see data in absolute contents in Fig. S3). Hence, these four OM fractions were considered to be the constituents of the bulk sedimentary OM hereafter. The relative proportion of various organic fractions showed down-core variabilities with sediment depth (Fig. 4).

At the deep site of Rappbode pre-dam, HCl hydrolyzable and H$_2$O$_2$ oxidizable OM consisted of more than 75% of TOC and of TN in sediments (Fig. 4). Variations in the composition of sedimentary OM in the upper 15 cm were revealed by corresponding decreases in proportions of HCl hydrolyzable carbohydrates and proteins. They decreased from 20 to 14% and 63 to 53% with respect to TOC and TN, respectively. In contrast, variation in the composition of sedimentary OM below 15 cm was linked to decreased H$_2$O$_2$ oxidizable lignins and lipids. The composition of sedimentary OM was found to be relatively stable at the shallow site of Rappbode pre-dam, only showing high values of four OM fractions in surface sediments (Fig. 4).

For the deep site of Hassel pre-dam, the relative percentage of HCl hydrolyzed OC and N in the upper 12 cm sediments decreased from 22 to 9% and 63 to 56%, respectively (Fig. 4). An additional decrease of Na$_2$S$_2$O$_8$ oxidizable lipids also contributed to the compositional variation in this depth interval (Fig. 4). OM composition in sediments below 12 cm changed as a consequence of the downward decrease of H$_2$O$_2$ oxidizable OM, which was 74 to 69% for OC and 32 to 29% for N between 12 and 22 cm (Fig. 4a). In contrast to the shallow site of Rappbode pre-dam, the composition of sedimentary OM at the shallow site of Hassel pre-dam changed appreciably in the depth interval of 10 to 14 cm, which was correlated with the decrease of hot water extractable OM (Fig. 4). Below 14 cm, the slight variation in OM composition resulted from gradual decreases of the other three OM fractions (Fig. 4).

**Isotopic alterations after sequential fractionation**

Sequential removal of sedimentary organic fractions also caused isotope fractionations in residual sediments. Hot water extracted 5–15% of OM from sediments, but it caused no significant variations in $\delta^{13}$C

| Sediment depth (cm) | Rappbode | Hassel |
|---------------------|----------|--------|
|                     | Deep     | Shallow | Deep     | Shallow |
| 0–2                 | 59.6 ± 13.9 | 30.3 ± 24.0 | NM | 57.0 ± 12.1 |
| 2–4                 | 62.5 ± 14.4 | 39.2 ± 20.9 | 69.5 ± 11.6 | 62.4 ± 11.8 |
| 4–6                 | 59.8 ± 15.4 | 34.9 ± 22.4 | 77.5 ± 11.8 | 62.2 ± 11.8 |
| 6–8                 | 63.1 ± 12.7 | 41.7 ± 20.0 | 81.5 ± 12.0 | 50.7 ± 12.6 |
| 8–10                | 64.9 ± 12.1 | 35.9 ± 22.0 | 58.5 ± 12.0 | 59.1 ± 12.9 |
| 10–12               | 68.7 ± 10.8 | 34.3 ± 22.6 | 57.3 ± 12.1 | 48.2 ± 12.9 |
| 12–14               | 66.5 ± 11.6 | 36.3 ± 21.9 | 46.5 ± 13.1 | 42.7 ± 13.6 |
| 14–16               | 64.7 ± 12.2 | 39.5 ± 20.8 | 55.5 ± 12.2 | 43.8 ± 13.4 |
| 16–18               | 66.2 ± 11.6 | 32.4 ± 23.2 | 53.0 ± 12.4 | 40.6 ± 13.9 |
| 18–20               | 65.3 ± 12.0 | 34.8 ± 22.4 | 59.5 ± 11.9 | 37.8 ± 14.3 |
| 20–22               | 68.4 ± 10.9 | NA | 59.4 ± 11.9 | NA |
| 22–24               | 53.6 ± 16.0 | NA | 43.1 ± 13.5 | NA |

The proportion was calculated from the two-source (terrestrial and aquatic) mixing model after Guillemette et al. (2017) (Eq. 1). Endmembers of C/N ratios for terrestrial OM sources are 15.4 ± 2.2 (n = 3) and 13.0 ± 0.9 (n = 3) for the Rappbode and Hassel pre-dams, respectively. Aquatic OM sources in the Rappbode and Hassel pre-dams have C/N ratios of 9.0 ± 0.1 (n = 2) and 8.7 ± 0.7 (n = 2), respectively. Variabilities of the relative contribution of algal-derived versus terrestrial-derived OM were calculated with endmember uncertainties using ‘propagate’ package in R.

NM Not measured, due to shortage of samples, NA Not available due to sediment core length.
and δ¹⁵N of hot water-resistant residues when compared to those of original bulk sediments (Fig. 5). In contrast, the removal of OM by HCl hydrolysis generated negative shifts of δ¹³C and δ¹⁵N. In addition, these isotope shifts differed substantially between sediment depths and sampling sites (Fig. 5). Compared to the shallow sites, overall larger shifts in sedimentary δ¹³C (t = 3.2, p < 0.01 for Rappbode pre-dam, t = 4.4, p < 0.0005 for Hassel pre-dam, Student’s t test) and smaller shifts in sedimentary δ¹⁵N
HCl hydrolysis-associated shifts in δ¹³C were often larger at the deep site of Hassel pre-dam than at the deep site of Rappbode pre-dam (t = −2.8, p < 0.05, Student’s t test).

Similarly, HCl shifts in δ¹⁵N were much larger in Hassel pre-dam (t = −3.1, p < 0.01, Student’s t test), which ranged between 0.9 and 2.7‰ compared to 0.2–1.8‰ in Rappbode pre-dam (Fig. 5b).

Removal of H₂O₂ oxidizable OM fraction only caused an evident shift in δ¹³C of surface sediments from the deep site of Hassel pre-dam, with an enrichment of up to 2.9‰ (Fig. 5a). Oxidation with H₂O₂...
produced more pronounced shifts in $\delta^{15}$N in sediments from Hassel pre-dam than from Rappbode pre-dam ($t = -3.1$, $p < 0.01$ for the deep sites, $t = -4.8$, $p < 0.0005$, Student’s $t$ test), with maximum shifts of 3.0‰ and 2.1‰ for the deep and shallow sites, respectively (Fig. 5b). After Na$_2$S$_2$O$_8$ oxidation, the residual sediments became enriched in $^{13}$C and depleted in $^{15}$N for all sampling sites.

**Characterization of sedimentary organic matter by $^{13}$C NMR**

Clear resonance peaks were found at the chemical shifts of 33 ppm, 133 ppm and 151 ppm with varying intensity in the $^{13}$C NMR spectra of the chemical resistant residues (Fig. 6). Integration results of these spectra (Table 3) indicated that the residual OM of HCl hydrolysis was dominated by alkyl and aromatic organic compounds. Besides, substituted alkyl and carboxylic compounds contributed in a relatively small proportion of OC in HCl-resistant residues. Residual OM of HCl hydrolysis in Rappbode pre-dam had a comparatively higher degree of aromaticity but lower degree of aliphaticity than sediments accumulated in Hassel pre-dam (Table 3). The HCl-resistant residues also differed between deep and shallow sites in terms of aliphaticity and aromaticity, i.e., sediments from the shallow sites of both pre-dams had higher abundance of aromatic compounds but lower abundance of aliphatic compounds (Table 3). These dissimilarities among sampling sites were eliminated after H$_2$O$_2$ oxidation through the removal of aromatic and carboxylic compounds, suggesting increasing homogeneity of OM in H$_2$O$_2$ resistant residues.

![Fig. 6 The $^{13}$C NMR spectra of HCl resistant residues (upper panels) and H$_2$O$_2$ resistant residues (lower panels) of sediment samples from Rappbode and Hassel pre-dams. Sediments used for $^{13}$C NMR analysis were collected from 14 to 16 cm depth at both deep and shallow sites of the two pre-dams](image-url)
### Table 3 Integration (in percentage) of $^{13}$C NMR spectra of HCl and H$_2$O$_2$ resistant residues

| Functional group    | Deep Rappbode | Shallow Rappbode | Deep Hassel | Shallow Hassel |
|---------------------|----------------|------------------|-------------|---------------|
|                     | HCl | $\text{H}_2\text{O}_2$ | HCl | $\text{H}_2\text{O}_2$ | HCl | $\text{H}_2\text{O}_2$ | HCl | $\text{H}_2\text{O}_2$ |
| Alkyl C (0–45 ppm)  | 50.7 | 73.4 | 38.9 | 75.9 | 52.9 | 70.8 | 47.7 | 72.8 |
| N-alkyl C (45–60 ppm) | 3.4 | 3.3 | 7.4 | 1.9 | 5.0 | 4.1 | 5.0 | 0.7 |
| O/O$_2$-alkyl C (60–100 ppm) | 11.0 | 7.0 | 12.1 | 7.5 | 12.1 | 9.6 | 9.8 | 7.2 |
| Aromatic C (100–145 ppm) | 18.8 | 6.7 | 24.5 | 6.4 | 13.4 | 5.4 | 20.2 | 8.0 |
| O-aromatic C (145–165 ppm) | 8.5 | 2.6 | 7.2 | 1.8 | 6.1 | 3.3 | 8.8 | 4.3 |
| Carboxyl C (165–215 ppm) | 7.6 | 7.2 | 10.0 | 6.5 | 10.6 | 6.7 | 8.4 | 7.0 |
| Aliphaticity        | 65.1 | 83.6 | 58.3 | 85.3 | 70.0 | 84.6 | 62.6 | 80.7 |
| Aromaticity         | 27.3 | 9.2 | 31.7 | 8.2 | 19.5 | 8.7 | 29.0 | 12.3 |

Samples were taken from the 14–16 cm depth interval of each sediment core.
Discussion

Dynamics of land- and algae-derived organic matter in sediments

Proportions of aquatic and terrestrial OM in sediments varied with depositional depth and exhibited spatial differences within and among reservoirs (Table 2). These variations indicate either changes in OM inputs or the specific degradation of organic components in sediments. Hassel pre-dam has comparatively less terrestrial OM, because of less leaf biomass from the agricultural catchment and higher biological production within the dam. It is marked by lower aromaticity of sedimentary OM (Table 3) and greater TOC and TN contents in suspended OM in Hassel pre-dam. Friese et al. (2014) also observed a higher chlorophyll-a concentration in the epilimnion of Hassel pre-dam than of Rappbode pre-dam, which supported a higher primary production in Hassel pre-dam.

In Rappbode pre-dam, proportion of aquatic OM in sediments at the shallow site stays almost constant throughout the sediment core (Table 2), which is well coupled to the stable down-core OM contents and stable isotope ratios (Fig. 2). These invariable compositions of OM sources suggest the recalcitrance and low bioavailability of terrestrial OM in reservoir sediments. The low microbial biomass determined supports this low bioavailability of OM at the shallow site (Table 1, Walter 2015). At the deep site, there is a ~9 mg g⁻¹ decrease of TOC content in the upper 10 cm sediments (Fig. 2). Meanwhile, the microbial C at the same site was indicated to decrease by 13 mg g⁻¹ from the surface to 10 cm in sediments (Table 1, Wendt-Potthoff et al. 2014), implying the consumption of OM by heterotrophic respiration.

Compared to Rappbode pre-dam, there is a more pronounced down-core decrease of aquatic OM the upper 15 cm (refers to the year of ~1990) of sediment cores in Hassel pre-dam (Table 2). As aquatic productivity is not likely to have increased in Hassel pre-dam since 1990, due to the reduced discharge of nutrients and decreased phytoplankton production in the reservoir system (Wentzky et al. 2018), the lower proportion of aquatic OM in the deeper sediments does not result from temporal decreases in aquatic inputs. Instead, such a substantial down-core decrease is probably caused by degradation of aquatic OM with higher N-availability that are easily consumed by microbes (Kaushal & Binford 1999; Khan et al. 2015), as Hassel sediments have a more than double microbial C content than Rappbode sediments (Table 1; Kloß 2013; Walter 2015; Wendt-Potthoff et al. 2014). Additionally, possible changes in the C/N ratio of algae, due to variations in phytoplankton community in the water column, might cause potential variations in bulk C/N ratios and thus contribute uncertainties to aquatic OM proportions in Table 2. Sediments at the shallow sites contain more terrestrial OM than the deep sites, because they are less influenced by in-situ biological production and receive more detritus from the catchment. Dadi et al. (2016) reported a three times higher sedimentation rate at the shallow site of Rappbode pre-dam, compared to the deep site, which might contribute to a larger amount of land-derived OM.

At the shallow site of Rappbode pre-dam, consistently high abundances of four OM fractions in the top 2 cm sediments (Fig. 4) may suggest increased sedimentation of terrestrial OM due extreme weather in recent years, e.g., frequent flooding in Germany from 2002 to 2011 (Kienzler et al. 2015). This interpretation is supported by higher proportions of terrestrial OM (Table 2) and coarser grains in surface sediments (Fig. S1). Elemental and isotope compositions of sedimentary OM below 2 cm showed little change over the course of deposition (e.g., the full sediment core showed by open circles, Fig. 7). This invariance indicates negligible degradation of OM after deposition and a constant terrestrial input as the sediments at the shallow site are dominated by terrestrial OM. The constant terrestrial input is consistent with the relatively consistent land use in the catchment. In contrast, gentle temporal variations in biochemical and isotope compositions of sedimentary OM are observed at the shallow site of Hassel pre-dam (Figs. 4, 7). Sediments in the upper 10 cm are more depleted in ¹³C and enriched in aquatic proteins and carbohydrates than sediments below. This trend is coherent with the depth-associated decreases of microbial C at this site (Kloß 2013). This observation suggests that bioavailable proteins and carbohydrates are consumed in the upper layer sediments.

Given the nutrient transports from the catchments declined dramatically in the last decades (Wentzky et al. 2018), aquatic inputs are expected to decrease as well in two pre-dams. Thus, the higher OC and N
contents in the upper layer sediments do not result from a higher productivity but are rather due to diagenetic reductions of deep buried sediments. A two-stage degradation of sedimentary OM seems to have occurred at the deep site of Rappbode pre-dam (two clusters of solid circles in Fig. 7a, b). This process is likely driven by a loss of aquatic proteins and carbohydrates in the upper 10 cm and a loss of lipids at depths below. Likewise, at the deep site of Hassel pre-dam, sedimentary OM increased towards a more terrestrial nature with depth (Fig. 7). Degradation of sedimentary OM starts with the loss of aquatic proteins and carbohydrates at 5 cm (Fig. 4). These compounds are preferentially consumed by microbes because of their freshness and enrichments of N- and S-containing compounds (Parkes et al. 1993). In the deeper part (below 12 cm), a substantial loss of H$_2$O$_2$-oxidizable lipids explains the observed decrease of sedimentary OM with depth (Fig. 4). Although H$_2$O$_2$ oxidizable OM also includes lignins, such a reduction of sedimentary OM is probably attributed to the decay of lipids and complex proteins. This preference is due to the fact that lignins are less likely to be degraded in sedimentary environments with low oxygen pressure and in the absence of fungi (Opsahl and Benner 1995), which are unavailable at the deep sites of pre-dams due to stratification.

Despite differences in degradation patterns, sediments from all sampling sites consistently show the importance of aquatic proteins and carbohydrates decomposition in the upper 15 cm with subsequent lipid decomposition in the deeper sediments. This finding demonstrates that proteins and carbohydrates become preferentially consumed under high microbial abundance. It also verifies that lipids are degradable after deposition. In general, aquatic- and terrestrial-originated lipids exhibit contrasting degradability (Muri et al. 2004; Robinson et al. 1984). For instance, physicochemical encapsulation within a mineral matrix might substantially decrease the degradability of terrestrial lipids, compared to aquatic lipids with the same chemical structure (Huguet et al. 2008). With the recalcitrance of terrestrial lipids, in addition to their relatively higher proportion of terrestrial OM in the deeper sediment of the deep site (Table 2), we propose that lipids of algal origin become preferentially degraded.

Depending on the intensity of microbial activities in the sediment column, the preferential degradation of organic components at the deep sites of pre-dams continues in the upper 15–20 cm sediments, because sedimentary OM is primarily consumed by bacteria during diverse metabolic interactions (Killops & Killops 2004). The deposited OC degraded by more than 20% in Rappbode pre-dam and for almost 40% in Hassel pre-dam during the deposition of the upper 20 cm of sediment. As sedimentation rate differs fundamentally among water bodies, it is essential to take proper time scales for deriving OC burial rates,
considering the possibly incomplete degradation of OM in sediments.

Variation in stable isotope ratios driven by preferential degradation

Degradation of sedimentary OM results in down-core decreases of TOC and TN contents and changes in the isotope and biochemical composition of sedimentary OM (Gälman et al. 2008; Zonneveld et al. 2010). Thus, indicators for OM sources, such as C/N ratio, $\delta^{13}C$ and $\delta^{15}N$ values, may also record the process of OM degradation over depth, and down-core variations in $\delta^{13}C$ and $\delta^{15}N$ values have to be considered carefully when identifying OM sources based on these isotopic proxies (Fig. 7). It is critical to determine whether isotopic variation reflect variable aquatic production or catchment discharge, or a preferential degradation of organic components. Relationships between biochemical compositions and stable isotope ratios provide essential information for the interpretation of these proxies.

Comparisons of isotope ratios of suspended POM and surface sedimentary OM suggest that aquatic OM is depleted in $^{13}C$ but enriched in $^{15}N$ relative to bulk surface sediments, while isotopic shifts after the sequential chemical treatments (Fig. 5) suggest that proteins and carbohydrates of aquatic and terrestrial origins are $^{13}C$- and $^{15}N$-enriched when compared to bulk sedimentary OM. The offsets in $\delta^{13}C$ and $\delta^{15}N$ values between HCl-resistant residues and original bulk sediments (Figs. 4, 5) further help to elucidate that proteins and carbohydrates of algal origin are $^{13}C$-enriched but $^{15}N$-depleted fractions in bulk sedimentary OM. These $\delta^{13}C$ features of specific organic components are in line with the stable carbon isotope compositions of planktonic compounds and sediments (Degens 1969). In addition, the downward increasing trends of $\delta^{15}N$ due to proteins and carbohydrates removal with depth confirm the negative correlation between the amino acid reactivity index and $\delta^{15}N$ values in sediment cores (Möbius et al. 2011).

In a similar manner, the $\delta^{13}C$ and $\delta^{15}N$ shifts related to the removal of lipids and lignins (Figs. 4, 5) suggest that lipids and lignins in sediments are $^{13}C$- and $^{15}N$-depleted with regard to bulk sedimentary OM. However, differences in changes of $\delta^{13}C$ and $\delta^{15}N$ depth profiles are observed among sampling sites, with noticeable $\delta^{13}C$ offsets only at the deep site of Hassel pre-dam (Fig. 5a) and clear $\delta^{15}N$ offsets at both deep and shallow sites of Hassel pre-dam (Fig. 5b). The greater negative $\delta^{15}N$ offsets compared to $\delta^{13}C$ offsets probably result from heterogenous distributions of lipids and lignins in sediments. In addition, sediments at the deep site of Hassel pre-dam are characterized by high aliphaticity (Table 3) and high abundance of $^{15}N$-enriched lipids of algal origin (Fig. 2). We therefore propose that aquatic lipids are $^{13}C$- and $^{15}N$-enriched relative to lignins on account of the larger $\delta^{13}C$ and $\delta^{15}N$ offsets when lignins are less abundant in sediments.

With the information about the isotope characteristics of specific organic components, the downward variations in stable isotope ratios can be better interpreted. The invariable down-core $\delta^{13}C$ values at the shallow site of Rappbode pre-dam (Fig. 5a) indicates a constant supply of terrestrial OC sources. For the deep site of Rappbode pre-dam, the depth profile of bulk sedimentary $\delta^{13}C$ (Fig. 2) mainly results from the reduction of $^{13}C$-depleted sedimentary OM of algal origin in the top 10 cm, and then the reduction of $^{13}C$-depleted lipids in sediments below. The corresponding increase in $\delta^{15}N$ (Fig. 2) indicates the preferential degradation of $^{15}N$-depleted proteins and carbohydrates of algal origin. Likewise, depth profiles of $\delta^{13}C$ and $\delta^{15}N$ (Fig. 6) are well coupled with the degradation kinetics of biochemical components (Fig. 5) in sediments of the Hassel pre-dam shallow site. However, we could not absolutely exclude the isotopic variations resulted from changes in C$_3$ and C$_4$ plant cultivation in the agricultural land of Hassel catchment. This effect is not suggested to contribute appreciably to these isotopic variations, since the deep coring site away from the inflow of terrestrial detritus (deep site) exhibits much more significant variations than the shallow coring site next to the inflow (shallow site).

Post-depositional degradation of sedimentary OM could yield appreciable shifts in the bulk stable isotope ratios to an extent that might obstruct signals of paleo-limnological proxies for the reconstruction of paleoclimate and paleoenvironment. When excluding substantial changes in the terrestrial and algal OM inputs to Rappbode pre-dam sediments, the ~2‰ positive excursions for $\delta^{13}C$ and $\delta^{15}N$ values in the deeper layers are likely a consequence of biochemical composition changes. These changes in turn result...
from preferential degradation of aquatic proteins and lipids. For studies in paleolimnology without considering the diagenetic modifications of stable isotope ratios, such a down-core increase of δ^{13}C and δ^{15}N values would be interpreted as changes in wet/dry climate and alternations between C_{3} and C_{4} plants (Meyers and Lallier-Vergès 1999), or in paleo-productivity associated with the trophic states of waters (Ahmad and Davies 2017; Bertrand et al. 2010).

A portion of the temporal variability of stable isotope ratios could be driven by the varying intensity of post-depositional alterations during early diagenesis. Similar to the deep site of Hassel pre-dam, dramatic enrichments of ^{13}C and ^{15}N observed in sediments might be attributed to diagenetic alterations during the early years of deposition in eutrophic water bodies (Gallent et al. 2020). Therefore, proper attribution of isotope alterations via preferential degradation of OM in local sediments are encouraged when reconstructing paleo-environments. Temporal and regional conditions, such as depositional settings, terrestrial versus aquatic OM compositions in sediment cores, trophic state of the study lakes or reservoirs and OC burial rate, have to be considered for a strict interpretation of these isotopic paleolimnological proxies.

Land-use related differences in degradation regime of sedimentary organic matter

Catchment land use of lakes and reservoirs have profound impacts on the terrestrial OM and nutrient inputs to waters (Leavitt et al. 2006), aquatic productivity (Botrel et al. 2014), planktonic community (Friese et al. 2014) and the depositional environment including redox condition, temperature and microbial activities in sediments (Guecker et al. 2009). Land use thus influences the sources, sedimentation and degradation of OM in reservoirs. Hassel and Rappbode pre-dams have similar hydrological and morphometric settings but different catchment land-use categories. These differences could help outline different land use influences on OM compositions. Comparisons of OC and N contents of fractionated OM between deep and shallow sites and between two pre-dams demonstrated noticeable spatial variabilities in the composition of sedimentary OM.

Sediments at both deep sites of the two pre-dams had higher proportions of proteins and carbohydrates as well as lipids and lignins than sediments at both shallow sites. For these two deep sites, sediments in Hassel pre-dam were more enriched in aquatic proteins, carbohydrates and lipids, than in Rappbode pre-dam. For the shallow sites, a larger quantity of proteins and carbohydrates was found in Hassel pre-dam while more lignins and lipids accumulated in Rappbode pre-dam. These spatial variabilities reveal differences in both OM sources and post-depositional transformations.

Sedimentary OM in mesotrophic Rappbode pre-dam is characterized by high C/N ratios (Fig. 3) and high aromaticity (Table 3). This observation confirmed a high proportion of lignins. Because lignins largely remain inaccessible to microbes, they have long been taken as indicator for terrestrial OM transported to lakes and reservoirs (Gough et al. 1993; Hedges & Mann 1979). A higher proportion of forests in Rappbode catchment deliver refractory and highly transformed plant remnants to the pre-dam, therefore, sedimentary OM in Rappbode pre-dam exhibits relatively low degradability. Our biochemical and isotopic analyses indicate less variable downward trends of sedimentary OM in Rappbode pre-dam (Figs. 4, 5), which implies that paleo-proxies in such geochemical settings can be better used as tracers for paleoenvironment.

By contrast, the eutrophic Hassel pre-dam, which receives a large quantity of nutrients from the more agriculture-influenced catchment, has higher sedimentary δ^{15}N values, high aquatic productivity and thus substantial amounts of algae-derived proteins and lipids in sediments (Fig. 4). Since heterotrophic bacteria in sediments favor fresh aquatic lipids, proteins and polysaccharides during early diagenesis, sedimentary OM in Hassel pre-dam, particularly at the deep site, is subjected to intensive degradation. Preferential degradation of OM could bring potential bias for estimation of contemporary OC burial rates and interpretation of paleo-proxies in eutrophic waters such as Hassel pre-dam. The averaged OC burial rate is estimated to be 410 g C m^{-2} y^{-1} at the deep site of Hassel pre-dam since the construction of pre-dams, representing water bodies of medium to high OC burial rates according to the estimation of Downing et al. 2008. Hence, impacts by agricultural activities in the catchment are not necessary for higher OC burial rates in eutrophic lakes and reservoirs, which might differ from the increasing OC burial rates with eutrophication in
natural lakes of lower sedimentation rates (Anderson et al. 2020; Heathcote et al. 2015).

Inconsistencies in degradation patterns associated with catchment land use may be attenuated at the shallow inflow sites of pre-dams, which exhibit low primary productivity (Dadi et al. 2017; Fortino et al. 2016), high flow velocity and turbidity. In addition, OM in the coarse detritus (see sediment grain size distribution in Fig. S1), which is transported to the shallow sites, usually has low bioavailability. Therefore, terrestrial detritus does not stimulate microbial growth and is not readily utilized by microbes as a carbon source in the sediment. Consequently, post-depositional OM degradation is inactive in freshwaters that receive high proportions of terrestrial OM.

Conclusions

Effects of post-depositional processes on OM preservation and isotopic paleo-proxies have been evaluated by comparing the biochemical and isotope compositions of sedimentary OM, in two adjacent freshwater reservoirs with different catchment land use. The eutrophic reservoir was more enriched in algae-derived proteins, carbohydrates and lipids and underwent more intensive mineralization, while the mesotrophic reservoir contained relatively more recalcitrant lignins that were less degradable. A preferential consumption of aquatic proteins and carbohydrates over lipids was observed in both reservoirs, particularly at the deep site of the eutrophic reservoir. These preferences resulted in post-depositional alterations of δ13C and δ15N values, which varied among sampling sites with different sedimentation and deposition settings. Eutrophic waters are exposed to more intensive post-depositional degradation of OM and modification of paleo-proxies than those in a lower trophic state, due to the larger fraction of aquatic OM. Catchment land use is intrinsically responsible for the diverse OM degradation patterns, primarily owing to its controls on the quantity and quality of deposited OM. Moreover, down-core variations of δ13C values reflect variable terrestrial and aquatic OM inputs, while the impact of preferential degradation on the initial sedimentary δ15N values outweighs any impacts from the variability in OM delivery to the lake. These complexities may hinder the estimation of OC burial rate in modern waters, and paleo-environmental reconstructions based on stable isotopes.

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