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 consequential carbon burial. This process also often causes diagenetic alterations on paleoenvironmental proxies. Yet, mechanisms behind the degradation of sedimentary OM and the depth-related variations in stable isotope ratios can only be explained in part. Degradation of sedimentary OM in two drinking water reservoirs with contrasting trophic states (eutrophic versus mesotrophic) and catchment land-use (agriculture versus forestry) were studied with a combination of typical chemical treatments to group sedimentary organic matter into four different biochemical fractions, i.e., carbohydrates, proteins, lignins and lipids. Our results show that the degradation of sedimentary OM was mainly driven by preferential degradation of aquatic proteins and carbohydrates. In a subsequent step, lipids seemed to be degraded. This process entails more pronounced reduction of sedimentary OM and associated depth variations in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in the eutrophic reservoir of agricultural catchment, when compared to the mesotrophic reservoir with a forest dominated catchment. Moreover, changes in the relative proportions of biochemical components in sedimentary OM have more pronounced impact on $\delta^{15}\text{N}$ isotope values relative to the ones of $\delta^{13}\text{C}$. Our findings also suggest that algae-derived OM is primarily responsible for the post-depositional alterations of elemental and isotopic compositions of sedimentary OM. This may be of importance for estimates of carbon sinks in lakes and reservoirs.

Introduction

Despite being relatively small in surface area and primary production compared to the oceans, freshwaters accumulate a large quantity of carbon in the water column and sediments (Tranvik et al. 2009). This accumulation is mostly due to high carbon sedimentation and burial rates. In particular, reservoirs sequester about 160 Tg organic carbon (OC) annually in their sediments (Dean & Gorham 1998). Such a high OC burial rate in reservoir sediments is mainly attributed to large terrestrial organic matter (OM) inputs that in turn result 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 biogeochemical degradation, which turns most reservoirs into strong methane emitters (Beaulieu et al. 2020; Deemer et al. 2016). Recent estimates on methane ebullition have 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 is intensely related to the degradation dynamics of OM in sediments. Moreover, degradation of sedimentary OM has the potential to modify the initial compositional and isotopic features of OM (Freudenthal et al. 2001; Lehmann et al. 2002). This in turn hampers the interpretation of down-core signals of biogeochemical proxies. Such proxies are commonly used for tracing OM sources and help to reconstruct climate and land-use patterns of the past (Braig et al. 2013; Torres et al. 2012). Thus, biochemical investigations of degradation patterns of sedimentary OM in the sediments are crucial for improving estimates of carbon sequestered in sediments and also allows for more reliable reconstructions of the paleoenvironment.

Multiple factors determine the regimes and paces of sedimentary OM degradation. They associate with geography, hydrology, morphology and catchment land-use of the lakes and reservoirs (Berberich et al. 2020; Darrow et al. 2017), as they influence the primary production and trophic states in the water column and degradability of allochthonous OM. Besides its sources (aquatic versus terrestrial), original composition and thermodynamic characteristics of OM (Fabiano et al. 1995; Tittel et al. 2019), conditions of the depositional environments, including microbial biomass and community (Boetius & Lochte 1994), redox conditions (Nierop et al. 2017) and temperature, also exert impacts on the degradation of OM in sediments. 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 (Gupta et al. 2007; Middelburg 2018). Such alterations are mostly caused by preferential degradation of labile organic components.

Degradation of sedimentary OM is studied either to evaluate the magnitude of sedimentary carbon sink or to trace processes of OM oxidization, transformation and preservation. 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 through various combinations of chemical extractions to address specific target organic components. However, most existing methods cannot entirely identify all organic components in sediments, and usually proportions of characterizable OM decreases with depth and thus obstruct the characterization of OM. The degradation rate of OM is conventionally determined by directly quantifying the down-core decrease of OM contents, or by measurements of oxygen consumption or CO₂/methane emissions from in-situ or incubation experiments (Guérin et al. 2008; Hulthe et al. 1998). In recent decades, a variety of biogeochemical models of broad spatial and time scales, such as G-type, power and continuum models, have been developed to illustrate the dynamics of sedimentary OM degradation (Boudreau 1996; Thullner et al. 2005). While these approaches can be informative, they often fail to address variable degradation kinetics among organic components, due to complex processes involved in OM degradation.

Overall, mechanisms of OM degradation show strong regional disparity and thus have not been well established in diverse water types such as oceans, rivers and reservoirs in high or low latitudes. Here, we present data of OM processing in two freshwater reservoirs with contrasting trophic states with the aim to clarify their OM's diagenetic fate. The different trophic states result from differences in land use and allow to study two contrasting reservoirs in the same climate setting. The objectives of our study were

- (1) to explain OM degradation and preservation dynamics that cause carbon respiration and burial;
- (2) to investigate depth-related variations in stable isotope ratios of sediments that are related to early diagenesis, and
- (3) to outline impacts of catchment land-use on sedimentary OM degradation mechanisms.

The setting of this study in a mid-latitude is representative for a large group of reservoirs worldwide that are placed in variable and changing land use scenarios.

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 (the Rappbode Reservoir System) in Germany. The Hassel and Rappbode pre-dams are impoundments reconstructed from two tributaries in front of the main reservoir in the 1960s. They serve as sedimentation basins for the reduction of particle and nutrient loads (Frieese et al. 2014). The Hassel pre-dam has a surface area of 0.26 km² and an impounding capacity of 1.64 Mio 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. The sub-catchment of Hassel pre-dam covers 44.6 km² with almost equal share of forest, cropped land and grassland area. The 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 Mio m³), mean and maximum depths (5.7 m and 17.0 m, respectively) and catchment area (47.6 km²). The catchment of the Rappbode pre-dam consists of 72 % of forest, 22 % grassland and almost no agricultural land (Wendt-Potthoff et al. 2014). Differences in the coverage of agriculture lands between the Hassel and Rappbode pre-dam catchments lead to contrasting trophic states in these two pre-dams and can be preserved in sediments accumulated over past few decades.

Sediment cores were collected from four sites, two in mesotrophic Rappbode pre-dam and two in the eutrophic Hassel pre-dam. In the Rappbode pre-dam, a shallow sampling site (51.70°N, 10.79°E, 4 m in water depth) was located near the inflow, and a deep sampling site (51.71°N, 10.80°E, 14 m in water depth) was close to the main dam (Fig. 1). The shallow (51.70°N, 10.83°E) and deep sampling sites (51.71°N, 10.83°E) in the Hassel pre-dam have the same water depths (4 m and 14 m, respectively) and offer good systematic comparisons with the Rappbode pre-dam (Fig. 1).

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. Four replicate sediment cores were taken from each sampling site. 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 transferred into pre-weighted polypropylene plastic vials for freeze-drying. Dried sediments were ground with agate mortar. Before this, large pieces of plant detritus were picked out manually. Well-ground sediments were weighted and kept for subsequent measurements.

Suspended particulate organic matter (POM) in the water column was sampled to obtain general information about algae in the 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, the 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 the residual 1 L of concentrated water sample 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 the dry particulate material was ground for POM characterization. We assumed that the material was mostly made up of algae as supported by findings of Friese et al. (2014) and Barth et al. (2017), who worked at the same sampling sites.

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 hours as a mild extraction. The obtained 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 (Fig. 2), 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 the 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; H₂O₂ oxidizes lignins, lipids and some complex proteins; and Na₂S₂O₈ 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), which was coupled with 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 measurement. Sample weights were increased to 20 mg for H₂O₂- and Na₂S₂O₈-treated sediment residues in order to increase peak signals for isotope analyses, especially for ¹⁵N. Homogenized sediment residues were combusted into purified gases like CO₂, N₂, H₂, SO₂, after which CO₂ and N₂ were determined by EA and IRMS. The 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 atomic ratios in this work. Stable carbon and nitrogen isotope ratios ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) were presented in parts per mil (‰) with reference to Vienna PeeDee Belemnite (V-PDB) and atmosphere, respectively (Coplen et al. 2006; Kayler et al. 2011). The 1-s measurement precision was 0.1 ‰ for $\delta^{13}\text{C}$ and 0.2 ‰ for $\delta^{15}\text{N}$ based on repeat analyses (n=6) of well mixed bulk field samples (see Materials and methods in Liu et al. (2020)).

Two-source mixing model for sedimentary organic matter

Atomic C/N ratios 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 the 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 (Guillemette et al. 2017) was employed,

$$C/N_{\text{sediment}} = fC/N_{\text{terrestrial}} + (1 - f)C/N_{\text{aquatic}}$$

where f is the relative proportion of terrestrial OM in sediments; C/N_{sediment} , $C/N_{\text{terrestrial}}$, and C/N_{aquatic} are the atomic C/N of the bulk sediments, the soil from the catchment and algae in the euphotic zone of the reservoir, respectively. The mean soil C/N in Rappbode and Hassel catchments are 15.4 and 13.1, respectively (Schönfeldt 2013), and the algal C/N value in this study is derived from that of the suspended POM in reservoirs.

Chemical composition analysis using ^{13}C nuclear magnetic resonance

Preliminary isotopic measurements indicated the discrepancy of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ shifts between the treatments with HCl and H_2O_2 among different sampling sites. This discrepancy was pronounced for deep sediments below 10 cm. Therefore, both the HCl and H_2O_2 resistant residues of relatively deep sediments (14-16 cm) were analyzed by ^{13}C nuclear magnetic resonance (NMR) for chemical structure (Fig. 2) in order to interpret the site-specific shifts in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ after H_2O_2 oxidation. The 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). Aliphaticity and aromaticity of the sedimentary OM were taken as the areas of ^{13}C NMR spectroscopic integration between 0 and 100 ppm and 100 to 165 ppm, respectively.

Statistical analysis

Mean values and standard deviations of elemental and stable isotope compositions were calculated for sediment samples with replicates (see Fig. 2). 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, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of untreated bulk sediments were simulated by generalized additive models (GAM) with the R package “mgcv”. 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 the comparisons of the 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 in 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 isotopically depleted, with a mean $\delta^{13}\text{C}$ value of -31.5‰ and a mean $\delta^{15}\text{N}$ value of 4.2‰ . In contrast, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of suspended matter in Hassel pre-dam were on average -30.4‰ and 5.5‰ .

Depth profiles of carbon and nitrogen contents

The depth profiles of TOC content at the deep and shallow sites of Rappbode and Hassel pre-dams are shown in Fig. 3, based on the analysis of Generalized Additive Models. At the deep site of Rappbode pre-dam, the sedimentary TOC content decreased from 86.9 to 61.3 mg g^{-1} (Fig. 3). In comparison, the TOC content ranged from 106.9 mg g^{-1} in surface sediments to 56.6 mg g^{-1} in bottom sediments at the deep site of Hassel pre-dam (Fig. 3). 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. 3). The TOC profile at the shallow site of Hassel pre-dam was less variable, showing only a change from $\sim 63 \text{ mg g}^{-1}$ to $\sim 56 \text{ mg g}^{-1}$.

around 10 cm (Fig. 3). Overall, sediments at the shallow site of the Rappbode pre-dam were more abundant in OC relative to those of the Hassel pre-dam.

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. 3). At the deep sites, TN content decreased downward from 8.9 mg g^{-1} to 6.0 mg g^{-1} for the Rappbode and from 12.4 mg g^{-1} to 6.3 mg g^{-1} for the Hassel sediments (Fig. 3). However, the downward decreases of TN content in sediment core at both shallow sites were attenuated to less than 1 mg g^{-1} (6.5 to 5.3 mg g^{-1} for the Rappbode pre-dam and 6.9 to 5.7 mg g^{-1} for the Hassel pre-dam (Fig. 3). In addition, sediments in both deep and shallow sites of Rappbode pre-dam contained consistently less nitrogen than sediments in Hassel pre-dam.

Depth profiles of the stable carbon and nitrogen isotope ratios

Sedimentary $\delta^{13}\text{C}$ at the deep site of Rappbode pre-dam increased from -31.1‰ to -27.6‰ in the upper 18 cm and remained almost unchanged below (Fig. 3). This development was different in the Hassel pre-dam where the $\delta^{13}\text{C}$ values at the deep site underwent an increase of 3.7‰ in the top to 10 cm sediments (from -31.3‰ to -27.6‰) and then stabilized. Below 16 cm, the $\delta^{13}\text{C}$ value significantly decreased from -27.2‰ to -29.3‰ . Also, the $\delta^{13}\text{C}$ value-depth profiles at the shallow sites of these two pre-dams exhibited contrasting down-core trends. The $\delta^{13}\text{C}$ value was rather invariable in 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. 3).

A downward enrichment of ^{15}N was observed in sediments at the deep site of Rappbode pre-dam. The sedimentary $\delta^{15}\text{N}$ increased by 2.6‰ ($2.9\text{--}5.5\text{‰}$) over the top 22 cm and remained unchanged below of this depth. In contrast, sediments at the deep site of Hassel pre-dam were more enriched in ^{15}N . The $\delta^{15}\text{N}$ value showed an increase from 4.5‰ in the top part of the core to 6.8‰ at 10 cm depth and followed by a moderate fluctuation from 18 cm to the bottom (Fig. 3). At both shallow sites, sedimentary $\delta^{15}\text{N}$ exhibited higher depth variability when compared to $\delta^{13}\text{C}$. However, based on a Student's t-test on the depth profiles of $\delta^{15}\text{N}$ for these two shallow sites, sediments of Hassel pre-dam were significantly more enriched in ^{15}N when compared to sediments of Rappbode pre-dam ($p < 0.0001$).

Compositions of aquatic versus terrestrial organic matter in sediments

C/N ratios of suspended OM were 9.0 and 8.7 for the Rappbode and Hassel pre-dams, respectively (Fig. 4). These values are lower than those of sedimentary OM. Overall, sediments in Rappbode pre-dam had greater C/N values than sediments in Hassel pre-dam (Fig. 4). This was also evidenced by statistical differences in C/N ratios between two deep sites or between two shallow sites (Student's t-test, both $p < 0.001$).

Deep site-sediments of both pre-dams underwent substantially down-core increases in sedimentary C/N ratios, of which, the maximum rate of increase in Rappbode pre-dam was not as pronounced as that in Hassel pre-dam (1.2 versus 1.7). Moreover, the increase of C/N ratios in Rappbode pre-dam mainly occurred at depths below 20 cm, while the increase of C/N ratios took place from 8 to 14 cm in Hassel pre-dam (Fig. 4). The highest C/N ratio was found at the shallow site of Rappbode pre-dam among all the sampling sites, which ranged between 12.7 and 13.5 with no clear down-core trends. The depth profile of sedimentary C/N ratios at the shallow site of the 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 the terrestrial source in sedimentary OM was then acquired from the mixing model. At the deep site of the Rappbode pre-dam, sedimentary OM with algae origins consistently prevailed over that with land-plant origins throughout the core, while sedimentary OM at the shallow site was dominated by terrestrial OM (Table 1). At both deep and shallow sites of Hassel pre-dam, aquatic OM makes up a large share of sedimentary OM in the upper 10 cm. The relative proportion 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 1). However, this proportion decreased abruptly below, in particular at the deep site, with a drop from 80 % to 60 % (Table 1).

Table 1
Vertical distribution of aquatic organic matter (in percent) in sediments at the deep and shallow sites of Rappbode and Hassel pre-dams. The proportion was calculated from a two-source (terrestrial and aquatic) mixing model after Guillemette et al. (2017)

Sediment depth (cm)	Rappbode		Hassel	
	Deep	Shallow	Deep	Shallow
0–2	59.6	30.3	NM	57.0
2–4	62.5	39.2	69.5	62.4
4–6	59.8	34.9	77.5	62.2
6–8	63.1	41.7	81.5	50.7
8–10	64.9	35.9	58.5	59.1
10–12	68.7	34.3	57.3	48.2
12–14	66.5	36.3	46.5	42.7
14–16	64.7	39.5	55.5	43.8
16–18	66.2	32.4	53.0	40.6
18–20	65.3	34.8	59.5	37.8
20–22	68.4	NA	59.4	NA
22–24	53.6	NA	43.1	NA
NM = Not measured, due to shortage of samples.				

NA = Not available due to the length of sediment cores.

Chemical fractions of sedimentary organic matter

Depth profiles of biochemical composition

The sequential fractionation procedure defined four OM fractions (hot water extractable, HCl hydrolysable, H₂O₂ oxidizable and Na₂S₂O₈ 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 were left in the residual sediments after the entire sequential fractionation. 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 variability with sediment depth, which implies changes in the composition of OM in sediments (Fig. 5).

At the deep site of the Rappbode pre-dam, H_2O_2 oxidizable OM consisted of 54–68 % of TOC and more than half of TN in sediments (Fig. 5). The variation in the composition of sedimentary OM in the upper 15 cm was revealed by corresponding decreases in TOC and TN contents of HCl hydrolyzable OM fraction, which were 6.5 and 0.8 mg g^{-1} , respectively. A slight decrease in the proportion of $\text{Na}_2\text{S}_2\text{O}_8$ oxidizable OM also contributed partly on the variation in the OM composition. In contrast, variation in the composition of sedimentary OM below 15 cm was linked to the decreased contents of H_2O_2 oxidizable OC and N. 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. 5).

The downward trend in the composition of sedimentary OM at the deep site of Hassel pre-dam was similar to that observed at the deep site of Rappbode pre-dam, but more pronounced. The content of HCl hydrolyzed OC and N in the upper 12 cm sediments decreased by 13.7 mg g^{-1} and 2.1 mg g^{-1} (Fig. 5), respectively. An additional 5.9 mg g^{-1} decrease of $\text{Na}_2\text{S}_2\text{O}_8$ oxidizable OC also contributed to the compositional variation in this depth interval (Fig. 5a). The composition of OM in sediments below 12 cm changed markedly as a consequence of the downward decrease of H_2O_2 oxidizable OM, which led to a reduction of H_2O_2 oxidizable OC reaching 31.2 mg g^{-1} between 12 and 22 cm (Fig. 5a). Different from the shallow site of Rappbode pre-dam, the composition of sedimentary OM at the shallow site of Hassel pre-dam changed noticeably in the depth interval of 10–14 cm, which was correlated with the decrease of hot water extractable OM (Fig. 5). Below this depth interval, the change of OM composition resulted from gradual decreases of the other three OM fractions (Fig. 5).

Isotopic alterations after sequential fractionation

Sequential removal of the 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 $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of hot water-resistant residues when compared to those of original bulk sediments (Fig. 6).

In contrast, the removal of OM by HCl hydrolysis generated negative shifts of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, and these isotopic shifts differed substantially from sediment depth and sampling site. Compared to the shallow sites, overall larger shifts in sedimentary $\delta^{13}\text{C}$ (as high as 1.6‰, Fig. 6a) and smaller shifts in sedimentary $\delta^{15}\text{N}$ (up to 2.7‰, Fig. 6b) were found at the deep sites. Moreover, HCl hydrolysis associated shifts in $\delta^{13}\text{C}$ were often larger at the deep site of Hassel pre-dam than at the deep site of Rappbode pre-dam (Fig. 6a). Similarly, HCl shifts in $\delta^{15}\text{N}$ were much larger in Hassel pre-dam, which ranged between 0.9–2.7‰ compared to 0.2–1.8‰ in Rappbode pre-dam (Fig. 6b).

Removal of H_2O_2 oxidizable OM fraction only caused an evident shift in $\delta^{13}\text{C}$ below surface sediments from the deep site of Hassel pre-dam, with an enrichment of up to 2.9‰ (Fig. 6a). The oxidation with H_2O_2 produced more pronounced shifts in $\delta^{15}\text{N}$ in sediments from the Hassel pre-dam than from the Rappbode pre-dam (Fig. 6b), with maximum shifts of 3.0‰ and 2.1‰ for the deep and shallow sites,

respectively. After Na₂S₂O₈ oxidation, the residual sediments became enriched in ¹³C and depleted in ¹⁵N for all sampling sites.

Characterization of sedimentary organic matter by ¹³C NMR

Clear resonance peaks were found at the chemical shifts of 33 ppm, 133 ppm and 151 ppm with varying intensity in the ¹³C NMR spectra of the chemical resistant residues (Fig. 7). The integration results of these spectra (Table 2) indicated that the residual OM of HCl hydrolysis was dominated by alkyl and aromatic organic compounds. Besides, substituted alkyl and carboxylic compounds also 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 2). 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 2). These dissimilarities among sampling sites were eliminated after H₂O₂ oxidation through the removal of aromatic and carboxylic compounds, suggesting increasing homogeneity of OM in H₂O₂ resistant residues.

Table 2
Integration (in percentage) of ¹³C NMR spectra of HCl and H₂O₂ resistant residues

Functional group	Deep Rappbode		Shallow Rappbode		Deep Hassel		Shallow Hassel	
	HCl	H ₂ O ₂	HCl	H ₂ O ₂	HCl	H ₂ O ₂	HCl	H ₂ 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 depth interval of 14–16 cm 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. These variations indicate either changes in OM sedimentation 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 convinced by the lower aromaticity of sedimentary OM (Table 2) 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 upper Hassel pre-dam than the Rappbode pre-dam, which supported a higher primary production in Hassel pre-dam. Moreover, there is a more pronounced trend of aquatic organic matter degradation in Hassel pre-dam. This pronounced degradation is probably caused by higher N availability and higher biological activity that feed more microbes, as Hassel sediments have a more than twofold higher microbial C content than Rappbode sediments (Kloß 2013; Walter 2015; Wendt-Potthoff et al. 2014). 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.

The downward variations in the fraction of algal OM with depth can be largely corresponded to the extent of microbial activity in sediment core. We make this assertion because the input of terrestrial OM is considered to be roughly invariable based on the relatively stable percentage contribution of terrestrial OM at both shallow sites (except for the surface sediments in Rappbode pre-dam, Table 1), where sediments are more sensitive to changes in terrestrial OM input than the deep site. Besides, Wendt-Potthoff et al. (2014) and Kloß (2013) indicated a decrease of microbial C with sediment depth at both deep and shallow sites in Hassel pre-dam (from 71 to 33 mg g⁻¹ in the upper 10 cm at the deep site and 24 to 11 mg g⁻¹ in the top 5 cm at the shallow site), which outweighs the decrease of TOC in the same sediment layer. Given the fact that algae-derived organic compounds are preferentially consumed by microbes (Kaushal & Binford 1999; Khan et al. 2015), the abrupt increase of terrestrial OM in sediments near 10 cm at the deep site of Hassel pre-dam might result from the metabolic reduction of aquatic OM (Table 1).

Depth profiles of stable carbon isotope ratios of sediments can also reveal the downward dynamics of OM compositions with respect to aquatic and terrestrial sources. At the deep sites of both pre-dams, the $\delta^{13}\text{C}$ values of surface sediments are identical to those of the suspended OM in the overlying water column. The more negative $\delta^{13}\text{C}$ values in the upper 10 cm sediments at both deep sites of pre-dams (Fig. 3) presumably resulted from the enrichment of ¹³C-depleted algal OM, consistent with the source

identification results derived from the C/N ratio (Table 1). However, OM in the surface sediments at the shallow sites had $\delta^{13}\text{C}$ values 1.5 to 3.0‰ greater than those of suspended OM. Hence, the shallow sites are suggested to receive a larger terrestrial OM input from the catchment than aquatic OM from *in-site* production. As the algae-dominated suspended OM is relatively depleted in ^{13}C , the varying extents of downward increasing $\delta^{13}\text{C}$ values among these sampling sites (Fig. 3) thus indicate that aquatic OM underwent different degrees of degradation.

Sedimentary organic matter degradation

Degradation of sedimentary OM causes decreases of TOC and TN contents with depth and changes of the biochemical composition of sedimentary OM (Gälman et al. 2008; Zonneveld et al. 2010). The biochemical composition of sedimentary OM at the shallow site of Rappbode pre-dam showed little change over the course of deposition (e.g., the full sediment depth, Fig. 5). This indicates negligible degradation of OM after deposition. High abundances of four OM fractions in top 2 cm sediments and the following decreases in deeper sediments (Fig. 5) may indicate an increased sedimentation of terrestrial OM in recent years rather than the degradation of OM, similar to sediments at the depth of 17 cm. This interpretation relies on the higher proportion of terrestrial OM in top sediments (Table 1). In contrast, downward variations in biochemical composition of sedimentary OM were observed at the shallow site of Hassel pre-dam. Sediments in the upper 10 cm were more enriched in aquatic proteins and carbohydrates than sediments below. This trend is coherent with the depth-associated decrease of microbial C at this site (Kloß 2013), suggesting that bioavailable proteins and carbohydrates are consumed in deeper sediments.

A two-stage degradation of sedimentary OM seems to have occurred at the deep site of Rappbode pre-dam, being driven by loss of aquatic proteins and carbohydrates in the upper 10 cm and loss of lipids at depths below. Likewise, at the deep site of Hassel pre-dam, degradation of sedimentary OM starts with the loss of aquatic proteins and carbohydrates at 5 cm (manifested by the abrupt decrease in HCl hydrolyzable C and N, Fig. 5). These compounds are preferentially taken 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_2O_2 oxidizable OM explains the observed decrease of sedimentary OM with depth (Fig. 5). Although H_2O_2 oxidizable OM includes also lignins, such a reduction of sedimentary OM is probably attributed to the decay of lipids and complex proteins, due to the fact that lignins are unlikely degraded in sedimentary environments of low oxygen pressure and in the absence of fungi (Opsahl & Benner 1995). The degradation patterns of sedimentary OM can be therefore depicted (see Fig. 8).

Inconsistencies in OM degradation patterns between deep and shallow sites (Fig. 8) can be ascribed to the varying intensity of microbial activities in the sediment column, as sedimentary OM is primarily consumed by bacteria during diverse metabolic interactions (Killops & Killops 2004). Despite the difference in degradation patterns, sediments from all the sampling sites consistently show the importance of aquatic proteins and carbohydrates decomposition in the upper 15 cm with subsequent

lipids decomposition in the deeper sediment. This finding demonstrates that protein and carbohydrate are preferentially consumed under high microbial abundance. It also verifies that lipid is degradable after deposition. In general, aquatic- and terrestrial-originated lipids vary fundamentally in degradability (Muri et al. 2004; Robinson et al. 1984), and physicochemical encapsulation within mineral matrix might substantially decrease the degradability of terrestrial lipids compared to aquatic lipids with the same chemical structure (Huguet et al. 2008). Given the recalcitrance of terrestrial lipids, in addition to the relatively higher proportion of terrestrial OM in the deeper sediment of the deep site (Table 1), we thus propose that lipids with algal origins are principally degraded.

Variation in stable isotope ratios driven by sedimentary organic matter degradation

Comparisons of the isotope ratio 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 sequentially chemical treatments (Fig. 6) suggest that proteins and carbohydrates with both aquatic and terrestrial origins are ^{13}C - and ^{15}N -enriched compared to bulk sedimentary OM. However, offsets in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values between HCl resistant residues and original bulk sediments also decreases with the amounts of proteins and carbohydrates (HCl hydrolyzable OC or N fraction in Figs. 5 and 6). In view of the isotopic characteristics of aquatic OM sources, proteins and carbohydrates of algal origins in sediments of Rappbode and Hassel pre-dams are suspected to be ^{13}C -enriched but ^{15}N -depleted fraction in bulk sedimentary OM. These $\delta^{13}\text{C}$ features of specific organic components are in line with known ^{13}C -distribution patterns in plankton and sediments (Degens 1969). In addition, the downward increasing shifts of $\delta^{15}\text{N}$ due to proteins and carbohydrates removal with depth correspond to the known relationship between the amino acid reactivity index and $\delta^{15}\text{N}$ values in sediment cores (Möbius et al. 2011).

In a similar manner, removal of organic components by H_2O_2 oxidation (Fig. 5) and the related shifts of the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ depth profiles of residual sediments (Fig. 6) suggest that the lipids and lignins in sediments are ^{13}C - and ^{15}N -depleted with regard to bulk sedimentary OM. This is not surprising as lipids and lignins have long been considered to be isotopically depleted components in plants (Hobbie & Werner 2004) or sediments (Rieley et al. 1991). However, the shifts of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ depth profiles are distinct among sampling sites, with noticeable $\delta^{13}\text{C}$ offsets only at the deep site of Hassel pre-dam (Fig. 6a) and clear $\delta^{15}\text{N}$ offsets at both the deep and shallow sites of Hassel pre-dam (Fig. 6b). These differences in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ offsets are considered to be the consequence of spatially different distributions of lipids and lignins in sediments. Sediments at the deep site of Hassel pre-dam are characterized by high aliphaticity (HCl resistant residues in Table 2) and high abundance of ^{15}N -enriched lipids with algal origins (Fig. 3). We therefore further propose that aquatic lipids are ^{13}C - and ^{15}N -enriched relative to lignins on account of the greater $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ offsets when lignins are less abundant in sediments.

With the information on the isotope abundances of specific organic components, the downward variations in stable isotope ratios can be related to changes either in sources or in biochemical composition of sedimentary OM. For the deep site of Rappbode pre-dam, the depth profile of bulk sedimentary $\delta^{13}\text{C}$ (Fig. 3) mainly results from the reduction of ^{13}C -depleted sedimentary OM of algal origin in the top 10 cm and then reduction of ^{13}C -depleted lipids in sediments below. The corresponding increase in $\delta^{15}\text{N}$ (Fig. 3) indicates the preferential degradation of ^{15}N -depleted proteins and carbohydrates derived from algae. These findings are in accordance with our results derived from the biochemical composition analysis. Compared with the deep site, the $\delta^{13}\text{C}$ - and $\delta^{15}\text{N}$ depth profiles for the shallow site of Rappbode pre-dam maintain almost unchanged (Fig. 6), in line with the stabilized biochemical composition in sediment core (Fig. 5). Likewise, depth profiles of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (Fig. 6) are well coupled with the degradation kinetics of biochemical components (Fig. 5) in sediments of Hassel pre-dam shallow site.

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

Catchment land-use of lakes and reservoirs has profound impact on the terrestrial OM and nutrient inputs to waters (Leavitt et al. 2006), aquatic productivity (Botrel et al. 2014), planktonic community (Frieze et al. 2014) and on the depositional environment such as redox condition, temperature and microbial activities in sediments (Guecker et al. 2009), thereby influencing the sources, sedimentation and degradation of OM. Hassel and Rappbode pre-dams are under similar hydrological and morphometric settings but different land-use scenarios in their catchments, thus catchment land-use is closely correlated with the OM composition and dynamics in sediments. Comparisons of OC and N contents of fractionated OM between deep and shallow sites and between two pre-dams demonstrated the spatial variability in the composition of sedimentary OM.

Sediments at both deep sites of the two pre-dams had higher proportions of HCl extractable proteins and carbohydrates as well as H_2O_2 oxidizable lipids and lignins than sediments at both shallow sites (Fig. 5). For these two deep sites, sediments in Hassel pre-dam were significantly more enriched in HCl hydrolyzable ($p < 0.005$ for both OC and N contents) and H_2O_2 oxidizable OM, namely aquatic proteins, carbohydrates and lipids, than in Rappbode pre-dam (Student's t-test, $p < 0.005$ for both OC and N contents). Moreover for the shallow sites, a higher proportion of proteins and carbohydrates was found in Hassel pre-dam, compared to Rappbode pre-dam (Student's t-test, $p < 0.001$ for OC content and $p < 0.05$ for N content in HCl hydrolysable OM). These spatial variabilities reveal largely differences in OM sources and post-depositional transformations.

Sedimentary OM in mesotrophic Rappbode pre-dam is overall characterized by great C/N (Fig. 4) and high aromaticity (Table 2), demonstrating a high proportion of lignins. As lignins are able to escape from microbial decomposition and degradation, they have long been taken as indicator for terrestrial OM that are transported to lakes and reservoirs (Gough et al. 1993; Hedges & Mann 1979). Forests in the 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. 5 and 6). By contrast, the eutrophic Hassel pre-dam, which receives a large quantity of nutrients from the more agriculture-influenced catchment, shows great sedimentary $\delta^{15}\text{N}$ value, high aquatic productivity and thus substantial amounts of algae-derived proteins and lipids in sediments (Fig. 5). 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, intensively degrades to a comparative content to that in Rappbode pre-dam. In contrast to an earlier study that argued agricultural development causes an increasing carbon burial in sediments (Heathcote & Downing 2012), our results suggest non-fundamental changes in carbon burial from a geological perspective.

However, differences in degradation pattern associated with catchment land-use may also be attenuated at the shallow inflow sites of pre-dams, where the water column features low primary productivity owing to the light and nutrient limitations (Fortino et al. 2016; Karlsson et al. 2009), high flow velocity and turbidity and no stratification. In addition, OM in the coarse detritus of land plants, which is transported to the shallow sites, usually has low bioavailability, i.e., not favored by microbial growth, and deposits without enough microbial reworking in sediments. Consequently, sedimentary OM degradation patterns do not differ significantly between the shallow sites of Rappbode and Hassel pre-dams, despite the contrasting land-use in their catchments.

Conclusions

We compared the accumulation and degradation of OM in two adjacent freshwater reservoirs with different land use in their catchments. Sedimentary OM in both reservoirs consists primarily of aliphatic lipids and aromatic lignins and subsequently of proteins and carbohydrates. A preferential consumption of aquatic proteins and carbohydrates over lipids is also established in both reservoirs, particularly at the deep sites. However, the composition of sedimentary OM varies apparently between these two reservoirs. The eutrophic reservoir is more enriched in algae-derived proteins, carbohydrates and lipids, while the mesotrophic reservoir contains relatively more recalcitrant lignins. These differences are connected to the specific depth profiles of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values among sampling sites. Sequential degradations of ^{13}C -enriched and ^{15}N -depleted proteins and carbohydrates and then ^{13}C -depleted and ^{15}N -enriched lipids with algal origins have led to depth variations in isotope signatures of bulk sedimentary OM. The deep site of the eutrophic reservoir underwent the most pronounced isotopic variations among the r sampling sites. This difference is due to the most rapid and decided losses of aquatic OM in the upper sediments. Our analysis on the post-depositional alterations of initial sedimentary stable isotope ratios suggests that depth profiles of $\delta^{13}\text{C}$ reflect variable terrestrial and aquatic OM inputs, while the impact of preferential degradation on the initial sedimentary $\delta^{15}\text{N}$ is superior to that of a variance in OM sources.

Land-use in the reservoir catchments seems to be responsible for the distinct degradation patterns between the two studied reservoirs. They indicate more efficient degradation of sedimentary OM in the

eutrophic reservoir that is influenced by more agricultural lands. A higher proportion of agriculture in the catchment causes higher rates of aquatic production in the water column and is associated with the more rapid accumulation of algae-derived OM in sediments. This, in turn causes higher degradation rates of labile aquatic OM by intense microbial activities. In contrast, sedimentary OM in the mesotrophic reservoir with more forest in its catchment shows lower degradability because of relatively higher inputs of refractory terrestrial OM such as lignins. This is accompanied with reduced bioavailable OM for microbial metabolism. Sedimentary OM of reservoirs plays an important role in global in carbon cycling and our results confirm the significant influence of land use. Future evaluations of global carbon burial and paleoenvironment reconstruction should consider our findings.

Declarations

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Figures

Figure 1

Map of Germany and the Rappbode Reservoir System with land-use in the catchments of Hassel and Rappbode pre-dams. Black bold border lines show the catchment boundaries. Color-coded polygons represent various land-use types (data were provided by ATKIS1 DGM50 M745; Geobasisdaten© Vermessungsverwaltungen der Bundesländer and BKG (www.bkg.bund.de); map was created by ArcGIS). Red asterisk in the top left panel represents the study site. Red dots in the right panel represent sampling points, of which YR3 and YH3 were located at the deep sites, and YRI and YHF were located at the shallow sites near the inflow of the pre-dams

Figure 2

Simplified profiles of the Rappbode and Hassel pre-dams. Three replicates were collected for OM fractionation from the sediment depths marked with n=3, and only a single sample was taken for the rest depths (vertical axes do not scale the actual depths in the water column and in sediments). Sediments were analyzed for ^{13}C resonance spectrum and stable isotope ratios if the depths were marked with ^{13}C NMR, while the other sampling depths were analyzed only for elemental contents and stable isotope ratios

Figure 3

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 intervals for the given parameters of the predicted nonlinear correlation

Figure 4

Depth profiles of atomic carbon to nitrogen ratio of sediments and suspended matter in the surface water. Filled and open symbols represent sediments sampled from the deep and shallow sites of Rappbode and Hassel pre-dams. Asterisks represent suspended matter sampled from the surface water of pre-dams. Error bars indicate the standard deviation of three replicates

Figure 5

Depth profiles of (a) carbon and (b) nitrogen contents in extracted organic matter fractions of sediments at the deep and shallow sites of Rappbode and Hassel pre-dams

Figure 6

Depth profile of stable carbon (a) and nitrogen (b) isotope composition in original bulk sediments and chemical resistant residues. Sediments were sampled from cores at the deep and shallow sites of the Rappbode and Hassel pre-dams. Black, green, orange and purple and red lines with markers show depth profiles of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ for the original untreated sediments, hot water-resistant residues, HCl-resistant residues, H₂O₂-resistant residues, and Na₂S₂O₈-resistant residues, respectively. Error bars represent standard deviations (n=3)

Figure 7

The ^{13}C NMR spectra of HCl resistant residues (upper panels) and H_2O_2 resistant residues (lower panels) of sediment samples from Rappbode and Hassel pre-dams. Sediments used for ^{13}C NMR analysis were collected from 14-16 cm depth at both the deep and shallow sites of the two pre-dams

Figure 8

Scheme of changes in biochemical composition with depth in sediment cores of the mesotrophic and eutrophic reservoirs. The preferentially degraded compounds are specified; areas of the bars are in proportion to the contents of organic matter in sediments