SOURCE IDENTIFICATION AND SPECIFIC DEGRADABILITY OF PARTICULATE AND SEDIMENTARY ORGANIC MATTER IN RESERVOIRS

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Sometimes ever, sometimes never...

Passion and great idea also...

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Summary

Freshwaters and their sediments contain a substantial amount of allochthonous and autochthonous organic matter (OM). The turnover of this OM pool in the water columns and sediments plays a significant role in the regional and global carbon (C) cycle and in climate change. The mechanisms involved in OM turnover have not been well elucidated as they are controlled by numerous interactive factors exhibiting a high temporal and spatial variability. Moreover, OM in aquatic systems is inherently complex and its constituents have undergone varying degrees of degradation. Knowledge of whether and how these organic components are degraded or preserved is essential to understand the biogeochemistry of OM in aquatic systems.

This thesis aimed at 1) identifying the terrestrial and aquatic OM sources in reservoirs, 2) elucidating the degradation of OM in sediments at a biomacromolecular level in different depths. This was carried out at two study sites, Hassel and Rappbode pre-dam, which are part of the Rappbode Reservoir System in Germany. The identification of OM sources in sinking material and buried sediments was accomplished by using biogeochemical proxies, carbon to nitrogen ratio (C/N) as well as carbon and nitrogen stable isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$). These proxies were also applied to study the degradation of OM. Processes of the specific degradation of the main organic components (lipids, lignins, proteins and carbohydrates) in sediments were described by quantifying those components through a sequential chemical fractionation procedure.

This procedure combined four chemical fractionation methods, yielding a fraction of proteins and carbohydrates and a fraction of lipids and lignins. The new developed stepwise fractionation procedure enabled the determination of C and N contents as well as stable isotopic compositions of OM fractions of different stabilities. Furthermore, it confirmed that $\delta^{13}C$ and $\delta^{15}N$ can be used for indicating changes of biomacromolecular composition in sedimentary OM.

C/N ratio and $\delta^{15}N$ recorded effectively the accumulation and degradation of POM in the water column. Comparing C/N ratios and $\delta^{15}N$ values of sediment trap material with deposited sediments revealed that the trapped material contained more aquatic OM than the deposited material. The relative aquatic POM contribution to sediment trap material exhibited no evident seasonal trend in the mesotrophic Rappbode pre-dam. By contrast, sediment trap material in the

eutrophic Hassel pre-dam had a larger contribution of aquatic detritus in summer, which corresponded with a higher primary productivity in the water column.

Proportions of aquatic and terrestrial OM in sediments showed a large variability among the sampling sites in both pre-dams. Terrestrial OM accounted for 20-70% of total sedimentary OM in both pre-dams. The highest proportion was found in the surface sediments at the shallow site of Rappbode pre-dam, while the lowest proportion was observed at 6-8 cm depth in the sediments of the deep site of Hassel pre-dam. This distribution was mainly caused by a higher aquatic production in the overlying water column as well as a larger amount of microbial biomass in its sediments of the deep site. As revealed by ^{13}C nuclear magnetic resonance analysis, sedimentary OM in Hassel pre-dam was more aliphatic and less aromatic compared to that in Rappbode pre-dam. Within both pre-dams, a higher aromaticity was found at the shallow sites compared to the deep sites. The proportion of terrestrial OM generally increased with sediment depth due to the preferential degradation of aquatic OM. This trend was better observed at the deep sites relative to the shallow sites, because of the larger contribution of aquatic sources to the sediments.

The degradation of OM in sediments was caused largely by the decomposition of lipids, proteins and carbohydrates of aquatic origin. It demonstrated that aquatic sedimentary OM was less important as a Carbon sink in a long-term perspective. Moreover, the preferential degradation of ^{13}C-enriched but ^{15}N-depleted proteins and carbohydrates over lipids and lignins was confirmed in this work. Most of the OM degradation took place at the deep sites of both pre-dams, although a minor loss of labile OM was still detected at the shallow sites. Sedimentary OM in Hassel pre-dam was exposed to more intensive degradation compared to that in Rappbode pre-dam, due to a higher proportion of aquatic OM and a larger microbial biomass in the sediments of Hassel pre-dam.

Distinctions in stable isotope ratios between aquatic and terrestrial OM sources outweighed the differences in stable isotopic ratios among various organic biomacromolecular components. Hence, the alterations of stable isotope ratios in sediment cores reflect largely the changes of contributions of aquatic and terrestrial OM sources. They indicate the selective preservation of refractory OM components in the deeper layers of the sediment cores where aquatic OM has been largely degraded.

Two factors affect the quality and quantity of sedimentary OM: (1) the trophic state and (2) the depositional environment in water bodies. Accordingly, land use in the catchments and basin topography are primarily responsible for the different sources and degradation profiles of the sedimentary OM in the two pre-dams. Towards the first factor, agricultural activities in the catchment of Hassel pre-dam likely caused high nutrient inputs and thus high primary production and OM sedimentation rates in Hassel pre-dam. Compared to the sedimentary OM in Hassel pre-dam, sedimentary OM in Rappbode pre-dam was characterized by a larger proportion of lignins. This can be explained by the high forest coverage (70%) and less agricultural land use in its catchment. Concerning the second factor, the depositional environment, there was a larger amount of terrestrial OM with a lower OM degradability in sediments at the shallow sites.

This thesis contributes to the understanding of OM cycling processes in aquatic systems, and promotes the application of stable isotope ratios in tracing OM degradation processes in aquatic sediments. These new methods and findings are not restricted to freshwaters but can be extended to marine ecosystems.

Zusammenfassung

Süßgewässer und ihre Sedimente beinhalten erhebliche Mengen an allochthonem und autochthonem organischem Material (organic matter, OM). Der Umsatz dieses OM-Pools in der Wassersäule spielt eine bedeutende Rolle im regionalen und globalen Kohlenstoffkreislauf und für den Klimawandel. Über die Mechanismen des OM-Umsatzes ist bisher wenig bekannt, da sie von zahlreichen wechselwirkenden Faktoren kontrolliert werden, welche eine hohe zeitliche und räumliche Variabilität aufweisen. Zudem ist OM in aquatischen Systemen von Natur aus komplex und seine Bestandteile weisen unterschiedliche Zersetzungsgrade auf. Kenntnisse ob und wie diese organischen Verbindungen abgebaut oder konserviert werden sind essentiell um die Biogeochemie des OM in aquatischen Systemen zu verstehen.

Die vorliegende Dissertation zielte auf (1) die Identifikation von terrestrischen und aquatischen OM-Quellen in Talsperren und (2) die Aufklärung der Abbauvorgänge der organischen Verbindungen in den Sedimenten auf makromolekularer Ebene. Untersucht wurde dies an zwei Vorsperren, Hassel und Rappbode, welche beide zum Rappbode Talsperrensystem in Deutschland gehören. Die Identifizierung der OM-Quellen in absinkenden und abgesetzten Material wurde mittels biogeochemischer Proxies bewertet: Kohlenstoff-Stickstoff-Verhältnis (C/N) und stabile Isotope des Kohlenstoffs und Stickstoffs ($\delta^{13}C$ und $\delta^{15}N$). Diese Proxies wurden auch genutzt um die Zersetzung von OM zu untersuchen. Der spezifische Abbau der wichtigsten organischen Komponenten (Lipide, Lignine, Proteine und Kohlenhydrate) in den Sedimenten wurde durch die Quantifizierung dieser Komponenten mittels eines sequentiellen chemischen Fraktionierungsverfahrens beschrieben.

Dieses Verfahren kombinierte vier chemische Fraktionierungsmethoden, die eine Fraktion der Proteine und Kohlenhydrate sowie eine Fraktion der Lipide und Lignine ergaben. Das neu entwickelte stufenweise Fraktionierungsverfahren erlaubte die Bestimmung von C- und N-Gehalten sowie die Bestimmung der stabilen Isotope der unterschiedlich stabilen OM-Fraktionen. Weiterhin bestätigte sich, dass $\delta^{13}C$ und $\delta^{15}N$ dazu genutzt werden können Änderungen in der biomakromolekularen Zusammensetzung des OM in Sedimenten aufzuzeigen.

C/N-Verhältnis und $\delta^{15}N$ zeigten die wirksame Anreicherung und Zersetzung von POM in der Wassersäule. Ein Vergleich der C/N-Verhältnisse und $\delta^{15}N$-Werte von Material aus

Sedimentfallen und abgelagerten Sedimenten zeigte, dass das Material aus den Sedimentfallen mehr aquatisches OM enthält als das abgelagerte Sediment. Der relative Anteil des aquatischen POM am Sedimentfallenmaterial wies keinen saisonalen Trend in der mesotrophen Rappbode-Vorsperre auf. Im Gegensatz dazu zeigte das Sedimentfallenmaterial in der eutrophen Hassel Vorsperre im Sommer einen höheren Anteil an aquatischem Detritus, was mit einer höheren Primärproduktion einhergeht.

Die Anteile von aquatischen und terrestrischen OM in den Sedimenten zeigten eine hohe Variabilität zwischen den Probenahmepunkten in beiden Vorsperren. Terrestrisches OM trug zu 20-70% zum gesamten sedimentären OM in beiden Vorsperren bei. Der höchste Anteil wurde an der Oberfläche der Sedimente an der flachen Stelle der Rappbode-Vorsperre gefunden, wohingegen der niedrigste Anteil in einer Sedimenttiefe von 6-8 cm an der tiefen Stelle der Hassel-Vorsperre beobachtet wurde. Diese Verteilung wurde hauptsächlich durch die höhere aquatische Produktion in der darüber liegenden Wassersäule und durch die höhere mikrobielle Biomasse in den Sedimenten an der tiefen Stelle verursacht. Mittels ^{13}C-Kernspinresonanzspektroskopie zeigte sich, dass sedimentäres OM in der Hassel-Vorsperre aliphatischer und weniger aromatisch war als in der Rappbode-Vorsperre. In beiden Vorsperren wurde eine höhere Aromatizität an den flachen Probenahmestellen gefunden im Vergleich zu den tieferen Stellen. Der Anteil an terrestrischen OM stieg generell mit der Sedimenttiefe an, da vorrangig aquatischer OM zersetzt wird. Dieser Trend konnte an den tiefen Stellen deutlicher beobachtet werden als an den flachen Stellen, da dort ein höherer Beitrag von aquatischen OM vorlag.

Die Zersetzung des OM in den Sedimenten wurde größtenteils durch den Abbau von Lipide, Proteinen und Kohlenhydraten aquatischen Ursprungs bestimmt. Es konnte gezeigt werden, dass aquatisches sedimentäres OM als langfristige C-Senke von geringerer Bedeutung ist. Darüber hinaus wurde in dieser Arbeit die bevorzugte Zersetzung von ^{13}C-angereicherten und ^{15}N-abgereicherten Proteinen und Kohlenhydraten gegenüber Lipiden und Ligninen bestätigt. Die OM-Zersetzung fand überwiegend an den tiefen Stellen der beiden Vorsperren statt, obwohl eine geringe Abnahme des labilen OM auch an den flachen Stellen nachgewiesen wurde. Sedimentäres OM in der Hassel Vorsperre wurde stärker zersetzt als in der Rappbode-Vorsperre,

was auf einen höheren Anteil an aquatischen OM und einer höheren mikrobiellen Biomasse in den Sedimenten der Hassel Vorsperre zurück geführt werden Kann.

Unterschiede in den stabilen Isotopen-Verhältnissen zwischen aquatischen und terrestrischen OM-Quellen überwogen die Unterschiede der stabilen Isotopen-Verhältnisse zwischen organischen makromolekularen Komponenten. Somit spiegeln die Änderungen in den stabilen Isotopen-Verhältnissen in den Sedimentkernen größtenteils die Änderungen in den Verhältnissen von aquatischen und terrestrischen OM-Quellen wider. Sie zeigen die selektive Konservierung von refraktären OM-Komponenten in den tieferen Schichten der Sedimentkerne in denen aquatisches OM zu einem fortgeschrittenen Grad abgebaut ist.

Zwei Faktoren beeinflussen die Qualität und Quantität des sedimentären OM: (1) die Trophie und (2) der Ablagerungsraum im Gewässer. Dementsprechend sind die Landnutzung in den Einzugsgebieten und die Topografie primär für die unterschiedlichen Quellen und Zersetzungsgrade sedimentären OM verantwortlich. Landwirtschaftliche Aktivitäten im Einzugsgebiet der Hassel Vorsperre verursachten höhere Nährstoffeinträge und somit höhere Primärproduktion und OM-Sedimentationsraten in der Hassel-Vorsperre. Verglichen mit dem sedimentären OM der Hassel-Vorsperre, was das sedimentäre OM in der Rappbode-Vorsperre war durch einen höheren Anteil an Ligninen charakterisiert. Dies kann durch die hohe Waldbedeckung (70%) und gerinere Landwirtschaft in diesem Einzugsgebiet erklärt werden. Bezüglich des Ablagerungsraums wurde mehr terrestrisches OM mit einer geringeren Abbaubarkeit in den Sedimenten der flachen Stellen gefunden.

Diese Dissertation trägt zum Prozessverständnis des OM-Kreislaufes in aquatischen Systemen bei und zeigt die Anwendbarkeit stabiler Isotopen für die Nachverfolgung von Zersetzungsprozessen des OM in aquatischern Sedimenten. Die neuen Methoden und Erkenntnisse sind dabei nicht auf Süßgewässer beschränkt, sondern auch in marinen Ökosystemen anwendbar.

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List of Abbreviations and Acronyms

Al^{3+}	Aluminum ion
C	Carbon
CH4	Methane
C/N	Carbon to nitrogen ratio
CO_2	Carbon dioxide
CP/MAS-NMR	Cross polarization and magic angle spinning- nuclear magnetic resonance
CSIA	Compound-specific isotopic analysis
CV	Coefficients of variance
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EA-IRMS	Elemental analyzer-isotope ratio mass spectrometry
Fe	Iron
Fe^{3+}	Ferric iron
FTIR	Fourier transform infrared spectroscopy
GC/C/IRMS	Gas chromatography combustion isotope ratio mass spectrometry
H_2	Hydrogen
HCO_3^-	Bicarbonate
HF	Hydrofluoric acid
HCl	Hydrochloric acid
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfate acid
$KMnO_4$	Potassium permanganate
OC	Organic carbon
OM	Organic matter
PAHs	Polycyclic aromatic hydrocarbons
Py-GC/MS	Pyrolysis gas chromatography-mass spectrometry
PVC	Polyvinyl chloride
N/N_2	Nitrogen
$NaHCO_3$	Sodium bicarbonate
NH_4^+	Ammonium
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide

$Na_4P_2O_7$	Tetrasodium pyrophosphate
$Na_2S_2O_8$	Disodium peroxodisulfate
NO_3^-	Nitrate ion
P	Phosphorus
POM	Particulate organic matter
POC	Particulate organic carbon
RRS	Rappbode reservoir system
S	Sulphur
SO_2	Sulfur dioxide
SRP	Soluble reactive phosphorus
TOC	Total organic matter
UV	Ultraviolet
ZrO_2	Zirconium dioxide

Chapter 1 Introduction

1.1 Motivation

Inland waters, such as lakes and reservoirs, affect the global climate and play a significant role in carbon (C) and nutrient cycles via the turnover of organic matter (OM) (Clow et al., 2015; Mulholland and Elwood, 1982), although they cover less than 3% of the earth's surface area (Downing et al., 2006). The active production and degradation of OM in inland waters lead to an intensive absorption and emission of greenhouse gases (e.g. CO_2, CH_4) and thus indirectly affect the heat and energy budgets in the atmosphere (Tranvik et al., 2009; Walter et al., 2006). In addition, the mobilization and sequestration of OM in aquatic system determines the magnitude of carbon (C), nitrogen (N), sulfur (S) and phosphorus (P) sinks in the water basins (Gälman et al., 2008; Moran and Zepp, 1997; Williamson et al., 1999). Elucidating the biogeochemistry of OM, therefore, is essential for understanding how inland waters are involved in climate change and element cycling.

Sediments in lakes and reservoirs retain a considerable fraction of OM. This large OM fraction results from allochthonous inputs from the catchment as well as the efficient sedimentation and preservation of autochthonous OM. For instance, lakes accumulate 0.02-0.04 Pg organic carbon (OC) per year within sediments, being comparable to the accumulation rates in oceans (Dean and Gorham, 1998; Einsele et al., 2001; Engel and Macko, 2013). The accumulation rate of OC in the sediments of reservoirs is even 4 to 10 times higher than that in natural lakes (Clow et al., 2015; Mulholland and Elwood, 1982). Furthermore, the flocculation of dissolved organic carbon (DOC) can be a potential addition to the carbon sink in sediments (von Wachenfeldt et al., 2008; von Wachenfeldt and Tranvik, 2008).

A range of biological, physical and geochemical processes are taking place in water bodies. These processes either translocate or alter OM of terrestrial and aquatic origin, which leaves fingerprints in the sediment. Therefore, sediments and their biomarkers not only record the sources and distribution of OM but also archive the biogeochemical processes involved in OM turnover in the water column and sediments (Dauwe and Middelburg, 1998; Meyers, 2003; Meyers and Ishiwatari, 1993b). For example, changes in terms of the relative importance of algal and land plant-derived OM, OM degradation state, thermal and trophic conditions in aquatic

systems can be traced from the isotopic, elemental and molecular characteristics of sediments (Brenner et al., 1999; Meyers and Lallier-Vergès, 1999; Usui et al., 2006).

Sedimentary OM is rather diverse in terms of ages, atomic and molecular structures. The diversity of OM arises from the influences that are exerted by various factors such as land use in the catchments, the topography of the water basin, biological diversity and redox conditions in the water column and sediments (Engel and Macko, 2013; Meyers, 1994). There are two pre-dams that are similar in size, morphology, hydrology and catchment area in Rappbode reservoir system (Friese et al., 2014). Nonetheless, these two pre-dams differ substantially in land use in the catchment and have been assessed to be different in the trophic state (Rinke et al., 2013). These features imply that a comparison of OM turnover between two pre-dams can contribute to deciphering the impact of land use in the catchment. A pre-dam is constructed like a natural lake with a surface overflow (Cooke et al., 2016; Wendt-Potthoff et al., 2014). However, compared to natural lakes, pre-dams have higher sedimentation rates and relatively large catchment areas (Kimmel and Groeger, 1984; Knoll et al., 2003; Tranvik et al., 2009), also making it a promising study site for sediment analyses.

Quantifying the degradation of OM and explaining the spatial and temporal variability of degradation rates remains challenging. Difficulties arise from the complex and intertwined factors that control the degradation of OM at structural and molecular levels (Alderson et al., 2016; Blair and Aller, 2012; Canfield, 1994). Moreover, aquatic OM and terrestrial OM are characterized by different susceptibilities to degradation, and components in OM exhibit different degradation states (Arndt et al., 2013; Henrichs, 1992, 1993). These facts further complicate the OM degradation processes.

Although investigations on the sedimentary OM started in the 1950s (Orr and Emery, 1956; Vallentyne, 1957), they are more often carried out in oceans than in freshwaters (Freudenthal et al., 2001; Froelich et al., 1979; Henrichs, 1992; Zhang et al., 2014). Given that the chemical and physiological characteristics differ largely between lacustrine and marine environments, the sources and degradation processes of OM in sediments can be quantitatively and qualitatively differentiated (Capone and Kiene, 1988; Engel and Macko, 2013). Furthermore, most of the characterization on sedimentary OM is limited to bulk samples and individual compounds (Alderson et al., 2016). Sedimentary OM exists as a highly complex mixture of multiple sources

and numerous compounds which has been intensely reworked by a number of biogeochemical processes (Arzayus and Canuel, 2005; Hedges and Keil, 1995; Kristensen et al., 1995). Few studies research the spatial variation of biomacromolecular composition of sedimentary OM, and even fewer studies linked the variations of biomacromolecular composition to the alterations of isotopic compositions of sedimentary OM.

To identify the key processes and factors controlling OM degradation in sediments, more information about the distribution and degradability of the main organic components is needed. Therefore, more effective OM fractionation, powerful analyzing techniques as well as indicative biomarkers are needed for the quantification and qualification of sedimentary OM degradation.

1.2 Biogeochemistry of organic matter in aquatic system

Particulate organic matter (POM) and dissolved organic matter (DOM) exist in varying proportions in the water column and sediments. The biogeochemistry of OM in an aquatic system is summarized in **Fig. 1.1**. OM in lakes and reservoirs mainly originate from aquatic organisms (autochthonous) such as photosynthetic products and from land-derived plants (allochthonous) in the watershed. It can be mineralized into greenhouse gases (CO_2 and CH_4), exchanged between the water column and sediments, or transformed from the dissolved into particulate form and vice versa.

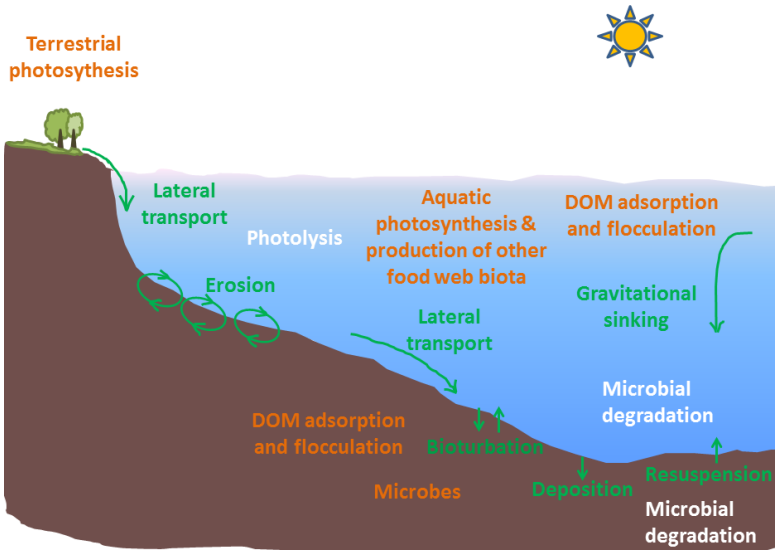


Fig. 1.1 Simplified diagram of the sources (orange), transport pathways (green) and transformations (white) of particulate organic matter (POM) and dissolved organic matter (DOM) in an aquatic system. After Meyers and Ishiwatari (1993a), Arndt et al. (2013) and Dadi (2016).

1.2.1 Production of organic matter

Despite terrestrial plants contributes considerable amounts of OM to freshwater ecosystems, most of the energy for the major biogeochemical processes is provided by photosynthesis in the euphotic zone (Niggemann, 2005; Summons, 1993). Aquatic photosynthesis is strongly dependent on light and nutrient availability (Petersen et al., 1997), and therefore, it is largely affected by water column depth, and by the surface area and latitude of the water basin (Knoll et al., 2003; Meyers, 1997; Tranvik et al., 2009). Moreover, anthropogenic factors such as intensive agricultural activities in the catchment can affect the primary production by discharging nutrients into the water basin (Anderson et al., 2013; Carpenter et al., 2001; Herczeg et al., 2001). In addition to photosynthesis, chemosynthesis, which oxidizes substrates in the deep water, is suggested to be a supplemental pathway for the OM production, even though it contributes a limited amount of OM compared to phytoplanktonic production (Taylor et al., 2001).

Secondary production is the process in which heterotrophic organisms, such as fishes, zooplankton, zoobenthos and heterotrophic microbes, use primary OM to generate biomass. In the presence of organic detritus, some microbes tend to consume instead of produce OM (Meyers, 1997). The structure of organic compounds and the stoichiometry of OM are often altered by the secondary production. Furthermore, this consumption of OM influences the energy flow, biodiversity, recruitment and biotic interactions in the water basin (Benke, 2010; Dolbeth et al., 2012).

1.2.2 Accumulation of organic matter

Both POM and DOM can accumulate in sediments. DOM diffuses into the deep water and sediments by thermoclinic or isopycnal transport (Pace and Prairie, 2005). It can settle down with particles via adsorption or aggregation (Barber, 1966; Druffel et al., 1996). However, the fate of settled DOM can be changed by desorption and incomplete mineralization of POM (Koelmans and Prevo, 2003). A majority of POM is rapidly recycled in the water column and sediments, and only a minority of initial OM can escape from biochemical modifications (Hodell and Schelske, 1998; Meyers and Ishiwatari, 1993a; Middelburg et al., 1993). In spite of the low sedimentation and deposition rates, POM is still the predominant constituent of the long-term Carbon sink in lake and reservoir sediments. This predominance of POM is more evident when

there is a large contribution of the allochthonous OM in sediments (Sobek et al., 2009). The sedimentation efficiency of OM are mainly controlled by microbial degradation in the water column, which itself largely depends on temperature, redox condition, deliver distance, quality of OM, microbial community, and nutrient loading (Ferland et al., 2014; Sobek et al., 2009).

OM near the water-sediment interface is likely to be re-suspended into the overlying water column, causing the further alteration and destruction of OM (Horppila and Nurminen, 2003; Koschinsky et al., 2001). Another important factor affecting the amount of OM in sediments is the flushing of OM through outlets in the water basin with human intervention. The impact of this factor is closely linked to the water withdrawal time, the hydrological regime as well as the diffusion and sedimentation rate of OM. The fraction of OM being flushed out the system is large in the pre-dams, especially under extreme weather conditions like flood events. Flushing furthermore regulates the nutrient elimination and thus influences the primary production and OM mineralization (Ulrich, 1997). Additionally, it exerts indirect influences on the flocculation and sedimentation of OM by changing the ratio of POM to DOM (Pütz and Benndorf, 1998; von Wachenfeldt et al., 2008; von Wachenfeldt and Tranvik, 2008).

1.2.3 Degradation of organic matter

Degradation of OM occurs in all compartments of the aquatic system, including the water column, water-sediment interface and sediments (Arndt et al., 2013; Meyers, 1997). It includes the overall degradation of OM by heterotrophic microbes via enzymatic and abiotic processes. Consequently, OM is oxidized or decomposed from macromolecules into small molecules (Pace and Prairie, 2005). The degraded OM is either utilized as an energy source or incorporated into biomass through biosynthesis. From the perspective of carbon cycling, OC is partly released as inorganic gases (CO_2, CH_4) (Alderson et al., 2016; Chmiel et al., 2016), and partly being preserved as a long-term carbon sink in aquatic systems (Last and Smol, 2006).

Environmental conditions, such as temperature, trophic state and the availability of oxygen, control the degradation of OM (Alderson et al., 2016; Anderson et al., 2014; Bastviken et al., 2004). The degradation rate of POM is 5-20 times higher than that of DOM in the water column (Sánchez‐García et al., 2011; van Dongen et al., 2008), although the DOC pool is usually 2-10 times larger than the POC pool (Tranvik et al., 2009). Degradation of OM, as a whole,

profoundly changes the mass and structure of OM. In freshwaters, approximate 83% of photosynthetic OM will be remineralized within the epilimnion (Eadie et al., 1984), and in total about 90% of original OM is degraded during sedimentation and deposition (Meyers and Eadie, 1993). In marine systems, the degradation rate can rise to 98% (Prahl et al., 1989). Thus, it is considered as a critical process in the recycling of OM and energy (Alderson et al., 2016).

Bacteria and zooplankton are the main consumers of OM. Therefore, the degradation of OM largely relies on aquatic environmental conditions which constrain the intensity of microbial and zooplanktonic activities. Overall, bacterial degradation is the prominent pathway to degrade and reshape OM in the water column and sediments. Jonsson et al. (2001) demonstrate that more than half of the OM in the water column is mineralized by bacteria, while zooplankton and photolysis together only consumed and degraded the remaining 40% of OM. Intense bacterial degradation of OM takes place also in sediments due to the ubiquitous occurrence of bacteria and diverse enzymatic reactions in sediments (Chróst and Siuda, 2006; Jackson et al., 1995; Meyer-Reil, 1984).

To measure and elucidate the degradation process, numerous approaches and techniques have been developed. There are three major categories: 1) monitoring the consumption or production of gas being produced by OM degradation (Hershey et al., 2015); 2) measuring the degradation of bulk OM via determining the reduction of elements (e.g. OC, N, S) or organic biomarkers in sediments (Stedmon and Markager, 2005); 3) using depth-resolving models that are established on the available understanding of the spatial distribution of OM and the key processes of OM degradation (Middelburg, 1989; Miller et al., 2009; Westrich and Berner, 1984).

1.3 Particulate organic matter in the water column and sediments

The biomacromolecular composition and degradability of POM in the water column differ conspicuously from those in sediments, due to varying OM sources and the biogeochemical alteration on OM during the sedimentation. Comparing POM properties between sediment trap material and sediments gives hints on the short and long-term degradation processes at different scales. In addition, it links the knowledge gap on OM degradation at the water-sediment interface.

Freshwater algae constitute a major fraction of POM in the photic zone of the water column, whereas land-derived POM, particularly in large detritus, can be buried more efficiently (Sobek et al., 2009). Dead algae are rapidly consumed by heterotrophic microbes or zooplankton as well as being slowly altered through chemical reactions. Accordingly, variations of POM in the water column to some extent reflect the seasonal and diel patterns of primary and secondary production.

Suspended particles (1-20 μm) not being captured by sediment traps consist of simple algal cells, detrital terrestrial fragments, bacteria as well as disaggregated organic particles (Engel and Macko, 2013; Meyers et al., 1984). They contribute only a limited OM fraction to the deep water and sediments (Baldock et al., 2004). Large sinking POM, which is easily sampled by sediment traps, is composed of large plankton, carcasses and feces of zooplankton, aggregates and flocculates that have been transformed from POM or DOM (Engel and Macko, 2013). POM undergoes resuspension and bioturbation at the water-sediment interface and is further exposed to post-depositional alterations (aerobic oxidation or fermentation) in sediments. Therefore, sedimentary POM below the bioturbated zone contains a comparatively larger proportion of refractory or well preserved organic compounds than suspended and sinking POM.

The quality and quantity of POM in sediments are determined by multiple factors in the water body and its catchment. Aquatic factors include OM transport distance, primary productivity, biological (bacterial, phytoplankton, zooplankton) community composition and the availability of electron acceptor in the water basin (Arndt et al., 2013). Terrestrial factors are, but not limited to, the land use and plant community in the catchment. For example, agricultural activities in the catchment not only alter the terrestrial POM input and molecular structure of organic compounds, but also increase the primary productivity in the water column and further change the contributions of algae to deposited POM (Anderson and Cabana, 2005; Herczeg et al., 2001; Woodward et al., 2012). POM transport distance in the water body, as another example, determines the sedimentation rate of POM (Dadi et al., 2015; Sobek et al., 2009) and simultaneously the exposure duration of POM to bacterial or zooplanktonic alteration (Meyers, 2003).

1.4 Biogeochemical proxies for particulate organic matter

Understanding the accumulation and alteration of POM in water basins facilitates the reconstruction of the paleoenvironment, the quantification of carbon burial as well as the associated biogeochemical processes. This identification can be accomplished by a combination of temporary monitoring with sediment traps and sediment core studies. Alterations in POM are marked within the bulk macro- and micro-molecular structures as well as isotopic compositions of the organic components. OM sources and their depositional environments can be traced with the help of these biomarkers.

1.4.1 Biomarkers

Biomarkers are relatively durable organic compounds whose structure and distribution in sediments archive extensive biogeochemical information (Alderson et al., 2016; Killops and Killops, 2013). The application of biomarkers allows the characterization of POM production, delivery and transformation in aquatic systems and can serve as a complementary measure. Typical biomarkers include lipids (Fahy et al., 2005a; Spooner et al., 1994), lignins and their derivatives (Derenne and Largeau, 2001; Norwood et al., 1987), pigments (Leavitt et al., 1989), polycyclic aromatic hydrocarbons (PAHs) (Baumard et al., 1998; Wakeham et al., 1997), ketones and esters together with some relatively labile compounds such as carbohydrates and amino acids (Dauwe and Middelburg, 1998; Marlowe et al., 1984). Meyers (1997) and de Leeuw et al. (2005) provide comprehensive reviews on the implication and limitation of various biomarkers.

Overall, biomarkers can be used to distinguish between aquatic and terrestrial sources and to trace OM diagenetic footprints. However, a biomarker is a fraction of an organic component, it thus provides only qualitative instead of quantitative information about OM origins and the degradation of sedimentary OM (Alderson et al., 2016; Meyers and Ishiwatari, 1993b). For this reason, biomarkers are more often applied in conjunction with sedimentary bulk indicators.

1.4.2 Bulk C/N ratios

Freshwater algae in lakes and reservoirs contribute substantially to the aquatic C pool in fresh sediments. They are cellulose-poor and protein-rich organisms and have thus relatively low

atomic C/N ratios ranging between 4 to 10 (Kaushal and Binford, 1999; Meyers and Ishiwatari, 1993b). Bacteria have C/N ratios typically between 4 and 6 as a result of the great abundance of protein (Khan et al., 2015). Compared with algae and bacteria, terrestrial land plants are evidently richer in cellulose and lignin and have accordingly greater C/N ratios (>20) (Keil et al., 1994; Meyers, 2003). OM in sediments is a mixture of algal, microbial and land plant detritus, therefore its C/N ratio is usually in the range of 10 to 20 (Das et al., 2013). Hence, the differences in C/N ratios among suspended, sinking and buried POM indicate the alterations of the relative contributions of algae and vascular land plants.

Besides the use in source identification, the alteration of C/N ratios can serve as an indicator of the OM degradation processes in sediments. The preferential degradation of nitrogen-containing organic compounds results in a larger proportion of carbon-enriched components in POM and consequently greater C/N ratios with the increasing sediment depth and burial time (Engel and Macko, 2013; Meyers and Eadie, 1993; Niggemann, 2005). Decreases of C/N ratios occur either when microbes incorporate inorganic nitrogen into new organic products, or when microbes selectively consume C-containing compounds (Khan et al., 2015). Continuous degradation of sedimentary OM during post-depositional period alters the original C/N ratio. Nevertheless, such a variation is slight compared to the differences of C/N ratios between aquatic and terrestrial OM sources (Meyers, 1997). In particular, C/N ratios of OM in lacustrine sediments can be better preserved and thus serve as a reliable biogeochemical indicator.

1.4.3 Carbon and nitrogen stable isotopic compositions

Carbon and nitrogen stable isotopic signatures ($\delta^{13}C$ and $\delta^{15}N$) are useful proxies for tracing OM sources and aquatic productivity (Meyers and Lallier-Vergès, 1999; Thornton and McManus, 1994; Woodward et al., 2011). In recent years, these proxies have been applied to reveal the sea level increases (Lamb et al., 2006) as well as changes in trophic state in aquatic systems (Bartoszek et al., 2016; McCutchan et al., 2003).

As aquatic plants assimilate dissolved nitrate (NO_3^-, $\delta^{15}N$ = 7‰ to 10‰), an isotopically heavy signature is incorporated into the new organic products. However, the inorganic nitrogen source for land plants is generally atmospheric N_2 whose $\delta^{15}N$ is about 0‰ (Schmidt and Gleixner, 2005). The assimilation of inorganic nitrogen, therefore, does not cause significant

isotopic fractionation, leading to a difference of approximately 8‰ in the $\delta^{15}N$ signatures of terrestrial plants and algae (Meyers, 2003; Meyers and Lallier-Vergès, 1999). Interpreting $\delta^{15}N$ values in aquatic environments can be a laborious task, since $\delta^{15}N$ values exhibit irregular alterations over the year. The difficulties arise from 1) the weak signature of $\delta^{15}N$, which consequently causes a relatively high deviation in the measurement; 2) more biological reactions are involved in the turnover of N than that of C in sediments (Talbot, 2002); 3) the high sensitivity of $\delta^{15}N$ to environmental changes and anthropogenic activities in the aquatic system and its catchment, all of which complicates the interpretation of $\delta^{15}N$ in the water column and the sediments (Lake et al., 2001; Teranes and Bernasconi, 2000).

Compared to the $\delta^{15}N$ value, sedimentary $\delta^{13}C$ values record effectively the cycling of OM and the availability of nutrients (Brenner et al., 1999; Gu et al., 1996; Lehmann et al., 2002). Inorganic carbon sources and photosynthesis pathways principally determine the carbon stable isotopic composition of sedimentary OM. A prevailing inorganic carbon source is CO_2 whose $\delta^{13}C$ value is approximately -7‰. An alternative carbon source is dissolved bicarbonate (HCO_3^-) with $\delta^{13}C$ values of about 0‰ (Teodoru et al., 2013). Atmospheric or dissolved CO_2 is preferentially used for OM production of land plants and freshwater algae because of the discrimination on heavy isotopes (Meyers, 1994, 2003).

In addition to the different carbon sources, the most evident discrepancy in $\delta^{13}C$ stems from the distinctive photosynthesis pathways. About 85% of plants on the earth use the C_3 pathway (Calvin cycle) to fix carbon. The remaining plants synthesize OM via the C_4 pathway (Hatch-Slack, a combination of PEP carboxylation and Calvin cycle) or the crassulacean acid metabolism (CAM) pathway (O'Leary, 1981). The different pathways discriminate against ^{13}C to various degrees and thus lead to distinctions in carbon stable isotopic fractionation. The isotopic fractionations caused by C_3 and C_4 pathways are generally -23‰ and -7‰, respectively (Mays et al., 2017). Hence, C_3 plants have $\delta^{13}C$ values around -27‰, and C_4 plants have $\delta^{13}C$ values ranging from -17‰ to -8‰ (Engel and Macko, 2013; Meyers, 1994).

The stable isotope ratios of carbon and nitrogen archive information that can be used, for instance, to trace energy flow (Yoshioka et al., 1994) and indicate lake productivity (Cole et al., 2002; Moschen et al., 2009). Likewise, the sedimentary nitrogen stable isotope ratio reveals the trophic state in water bodies, since it clearly correlates to the availability of NO_3^- in the water

column (Altabet and Francois, 1994). These two stable isotope ratios are more often used in conjunction with C/N ratios to serve as a more powerful tool to study the sources and turnover of OM as well as to reconstruct past aquatic environments (Woodward et al., 2011). Compositions of terrestrial C_3 plant-, C_4 plant- and phytoplankton-derived OM can be deduced from a combination of C/N ratio and stable isotope ratios (**Fig. 1.2**). Furthermore, numeric investigations have been carried out to explore the implications of these proxies for tracing paleoclimate and paleoenvironment changes (Das et al., 2013; Leng and Marshall, 2004; Torres et al., 2012).

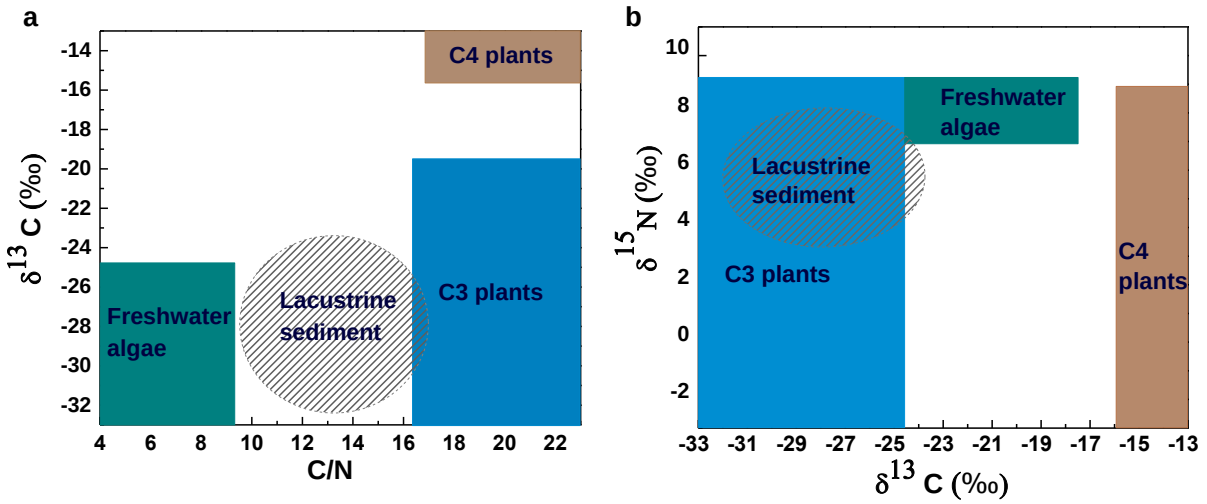


Fig. 1.2 a C/N and carbon stable isotope ratio in plants and the general values in lacustrine sediments. **b** Carbon and nitrogen stable isotope ratios in plants and the general values in lacustrine sediments. After Das et al. (2013) and Meyers (1997).

1.4.4 Compound-specific stable isotope ratios

Under the circumstances that bulk stable isotope ratios point to several potential origins of sedimentary organic compounds (Meyers et al., 1984), it is essential to utilize compound-specific isotopic analysis (CSIA) for obtaining further information on a molecular level. The CSIA of sedimentary organic compounds was begun in the 1990s (Hayes et al., 1990; Macko et al., 1990). Since then, it helped to refine the available information on ecological dynamics, organic sources biogeochemical recycling and trophic status in the aquatic system (Larsen et al., 2013). So far, compounds such as long-chain and waxy *n*-alkanes, pigments, lignin oxidized products, amino acids have been used frequently to trace the importance of various organisms for sedimentary POM (Filley et al., 2001; Mays et al., 2017; Naeher et al., 2016). Particularly, sedimentary amino

acid carbon and nitrogen stable isotope ratios are gradually considered as a novel and promising means to obtain precise information on nutrient utilization, as well as carbon and nitrogen cycles in aquatic environments (Batista et al., 2014; McCarthy et al., 2007; Pelz et al., 1998; Rieley et al., 1991).

1.5 Biomacromolecular components in sediments

Refractory components that are characterized by low degradability comprise lignins, sterols, *n*-alkanes (algaenans, cutans, suberans), waxes, tannins, alcohols. They are preserved by their intrinsic stability or due to the lack of organisms with specific enzymes that are able to perform degradation (Derenne and Largeau, 2001; Killops and Killops, 2013; Meyers and Lallier-Vergès, 1999). Simple carbohydrates, proteins, fatty acids, carbonyls, and pigments are highly degradable and termed as labile organic components in sediments (Fabiano et al., 1995; Silveira et al., 2008). Nevertheless, refractory components, such as lipids and lignins, are not absolutely immune from microbial attacks (Bianchi, 2011; Dittmar and Lara, 2001), and a fraction of labile organic components can resist rapid degradation through polymerization and encapsulation (de Leeuw et al., 2005; Gupta et al., 2007). The relative persistence of those biomacromolecular organic components in sediments is given in **Table 1.1**.

As a ubiquitous organic component, proteins occur as enzymes, carriers, regulators, and as functional units for nutrient storage as well as skeleton formation in organisms (Baldock et al., 2004; Engel and Macko, 2013). They are generally classified into hydrophobic (globular) and hydrophilic (fibrous) proteins. Globular proteins consist of enzymes, nutrient storage proteins and antibodies, of which antibodies are rather rare in sediments. Fibrous proteins, which have long stringy molecules, contribute a large fraction of OM to the sediments. Their existence in sediments is primarily due to the physical protection through encapsulation or absorption to clay minerals (Knicker and Hatcher, 1997). In addition, an alternative preservation mechanism is the neoformation of proteins into complex macromolecules through a Maillard reaction (Derenne and Largeau, 2001). They degrade intensively in the water column and represent only 3 to 8% of those originally produced by algae. However, the degradation rate of proteins within the sediments from the surface to 15 cm depth is determined to be about 50%, which is even lower than the degradation of lipids (Fichez, 1991).

Table 1.1 Occurrence and the expected main thermal degradation products of major organic constituents in organisms, as well as their degradability in the water column and sediments during sedimentation and diagenesis. After Tegelaar et al. (1989), De Leeuw and Largeau (1993) and Meyers (2003)

	Occurrence	Major catagenetic products	Biodegradability [a]
Lignins	Vascular plants	Condensed aromatics and CH_4	–
Tannins	Vascular plants	Condensed aromatics	–
Algaenans	Algae	n-alkanes and some aromatics	–
Cutans	Vascular plants	n-alkanes	–
Suberans	Vascular plants	n-alkanes and aromatics	–
Proteins	All organisms	Amino acids	+++/++
Celluloses	Vascular plants, some fungi	Unbranched polysaccharides	+++/++
Hemicelluloses	Vascular plants, some fungi and algae	Branched polysaccharides	+++/++
Sterols	Vascular plants, some fungi	n-alkanes and aromatics	++/+

[a] The degradability of each type of macromolecules was given on the basis of the chemical stability. Other mechanisms such as physical protection and microbial activities were not taken into consideration. The degree of degradability ranges from '–' (almost no degradation under any depositional conditions) to '+++' (extensive degradation during sinking and diagenesis).

Carbohydrates in vascular plants cells are present predominantly as starch and cellulose, which serve as carbon and energy storage substrates (Chróst and Siuda, 2006). Besides, algae and some bacteria also contain starch as well as other polysaccharides. Despite the high abundance of organisms, the content of carbohydrates in sediments is comparatively low. A majority of land plant carbohydrates is bioavailable and has transported over a long distance transport before arriving at the floor of the water basin, therefore allowing for the degradation and turnover over a long period (Baldock et al., 2004). Moreover, comparing with land plant carbohydrates, algal and bacterial-derived carbohydrates have less complex structure, lower molecular weights and thus higher susceptibility to enzymatic degradation. Starches in cyanobacteria, for example, were consumed by microbes within a few millimeters of the surficial sediments in Solar Lake in Egypt (Klok et al., 1984).

Lignin is the end product of metabolism and an important constituent of sedimentary OM. It originates from vascular plants, and exists as the second most abundant organic component after cellulose (on average 25% of total dry biomass). Coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol are the major phenylpropanoid units of lignins (Killops and Killops, 2013).

Depending on the dehydrogenative condensation of these phenylpropanoid units, gymnosperm, dicotyledonous angiosperm or monocotyledonous angiosperm lignins can be synthesized (Derenne and Largeau, 2001). Those lignins vary in bioavailability and stability. In general, they are relatively less susceptible to microbial reworking compared to the other organic components (Meyers, 1997). Their resistance partly attributes to the complex phenylpropanoid linkages as well as aromatic structures in lignins, and partly attributes to their indigestibility to plenty of microbial species. Fungi are the most effective organisms for lignin degradation (Killops and Killops, 2013). However, rapid and intensive fungal lignolysis needs high oxygen partial pressure (Szklarz and Leonowicz, 1986), which is not available in sediments.

Lipids are found in biological membranes as well as energy and biogeochemical information storage materials. They are categorized by their solubility instead of their structural functions (Van Meer et al., 2008). There are three main sources of lipids in aquatic ecosystems, including inputs from primary production, microbes, as well as terrestrial detritus from catchments (Silva et al., 2008). Mostly, they are extracted as fatty acids, *n*-alkanes, *n*-alkanols, ketones, sterols, alcohols and glycerols (Fahy et al., 2005b; Meyers, 1997). In addition to these biosynthetic constituents, PAHs are organic compounds which are yielded from diagenesis in sediments (Laflamme and Hites, 1978). These lipids occur in different abundances in organisms and differ largely in susceptibility to degradation. Overall, freshwater algae and bacteria are comparatively richer in lipids than land plants (Meyers, 2003; Ohlrogge and Browse, 1995; Stehfest et al., 2005). Short chain, oxygen-containing and unsaturated lipids, such as fatty acids with C=C bonds, have a higher susceptibility to microbial decomposition than the long chain, cyclic triterpenoids with high molecular weight (Killops and Killops, 2013; Meyers, 1997). Moreover, the freshness of lipids is proposed as an additional factor that affected the hydrocarbon contents in sediments, whereby the algal lipids are selectively degraded during the sinking and early diagenesis (Pinturier-Geiss et al., 2001).

1.6 Fractionation of sedimentary organic matter

Organic components in bulk sediments are diverse in sizes and chemical properties. Accordingly, they are accumulated and degraded at different rates in sediments (Baldock et al., 2004). Furthermore, the alteration or preservation of various components can be attributed to

different mechanisms, such as encapsulation, organo-mineral aggregation and chemical recalcitrance of organic compounds (Burdige, 2007; Poirier et al., 2000). These facts, on the one hand, weaken the power of the bulk geochemical indicators. For example, the $\delta^{13}C$ values of two sediment samples resemble closely, but they can have evidently distinctive biomacromolecular compositions. On the other hand, it might hinder the characterization of OM at a molecular level as OM presents as biopolymers (Alderson et al., 2016). To get an insight into OM accumulation and degradation processes, sedimentary OM is proposed to be separated based on the preservation mechanism or degradability of different organic components.

Numerous chemical, physical and combined fractionation procedures have been developed to isolate the organic species of interest or to separate bulk sedimentary OM into reduced fractions with specific properties. Due to the limited studies carried on sediments, this section will mainly focus on the available fractionation methods that have been applied to soil OM.

1.6.1 Physical fractionation

Physical fractionation methods are adopted for the separation of OM pools with the premise that OM turnover is largely controlled by the biological accessibility of organic substrates to microbes (Christensen, 2001; Wakeham and Canuel, 2016). These methods separate organic components based on their differences in particle size, mineral density or magnetic intensity. Therefore, particle size fractionation (Guggenberger et al., 1994; Sposito et al., 1999), density fractionation and magnetic fractionation (Kahle et al., 2003; Kaiser et al., 2002; Shang and Tiessen, 2000) are the most important approaches (Christensen, 1992; von Lützow et al., 2007). In this work, physical fractionation was not applied instead of chemical fractionation since the latter appeared to be more promising for the goal of this study.

1.6.2 Chemical fractionation

OM highly differs in solubility in various organic and inorganic solvents (Anderson and Paul, 1984; Schnitzer and Schuppli, 1989). In addition, it exhibits different resistances to chemical treatments, such as oxidation and demineralization (Rovira and Vallejo, 2002; von Lützow et al., 2007). Therefore, chemical fractionation approaches that based on these differences have a wide

diversity. In general, they are grouped into four major classes: hydrolysis, oxidation, mineral phase destruction and solvent extraction.

To isolate OM with comparatively high bioavailability, OM is generally hydrolyzed with hot water and acids such as hydrochloride acid (HCl) and sulfate acid (H_2SO_4) (Balesdent, 1996; Leavitt et al., 1996; Paul et al., 2006; von Lützow et al., 2007). Hot water extractable OC constitutes 1-7% of total soil or sedimentary OC, and it encompasses mainly microbial carbohydrates and N-containing compounds (Heller and Weiß, 2015; Leinweber et al., 1995). Acids are supposed to extract most of the carbohydrates and proteinaceous material, which is accomplished by disrupting the hydrolytic bonds without destroying the structures of other alkanes, alkenes and phenol aromatic hydrocarbons (Rovira and Vallejo, 2002; von Lützow et al., 2007). The proportion of OM extracted by acids largely varies with the physical and chemical properties of sediments, as well as the type and concentration of acids. For example, the variation of HCl hydrolyzable OM in soils between different layers of a sediment core is as high as 20% (Collins et al., 2000; Paul et al., 1997). Under the same operational conditions, HCl is more efficient in isolating carbohydrates, proteins and amino acids than H_2SO_4 (Rovira and Vallejo, 2002). However, the recalcitrance to acid indicates not exactly the turnover time of OM, as HCl hydrolyzable soil OM was detected to have an age of up to 5,500 years (Paul et al., 1997).

Isolation of the chemically refractory OM fraction is accomplished through the utilization of oxidizing agents. Typically, oxides like potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl), and disodium peroxodisulfate ($Na_2S_2O_8$) have been applied to OM fractionation (Blair et al., 1995; Jagadamma and Lal, 2010; Jagadamma et al., 2009; Menegatti et al., 1999). High-energy ultraviolet (UV) is also used as a complementary tool to separate the passive and active OM fractions (Skjemstad et al., 1993). $KMnO_4$ oxidation, which is similar to HCl hydrolysis, tends to oxidize active components such as polysaccharides and amino acids. It is a mild fractionation method of an oxidation rate in the range of 13-28% for agricultural soils (von Lützow et al., 2007). Wet oxidation with H_2O_2 is used to remove a fraction of OM which is susceptible to enzymatic degradation. O/N alkyl and aromatic compounds such as lignins are selectively oxidized by H_2O_2, whereas C-enriched aliphatic compounds and some pyrogenic material are resistant to H_2O_2 oxidation. The oxidation with $Na_2S_2O_8$ has been considered as a parallel fractionation procedure with H_2O_2 oxidation due to

similar oxidation efficiency. Nevertheless, $Na_2S_2O_8$ is more efficient than H_2O_2 in oxidizing aliphatic compounds (except long-chain alkynes and OM associated with minerals) (Jagadamma et al., 2009). NaOCl has been used frequently for the removal of soil OM, especially for humic substances. Yet, it is as a halfway oxidizing agent with an OM removal rate varying from 26% to 96% (Helfrich et al., 2007) and thus is deemed to be less effective than H_2O_2 and $Na_2S_2O_8$ oxidation.

Organo-mineral destruction by hydrofluoric acid (HF) or dithionites is suggested to be a particular approach for sample pre-treatment. HF is utilized to isolate the fraction of OM associating with minerals from the fraction that is free of association with minerals. It dissolves hydrated silicate minerals and yields either ferruginous or aluminiferous complexes (Eusterhues et al., 2007; von Lützow et al., 2007). Demineralization with dithionite is based on the destructions of Al^{3+}-Fe^{3+} bonds between OM and clay minerals, and it extracts primarily aliphatic and carboxyl compounds and some sugars (Dai K'o and Johnson, 1999).

Solvent extractions isolate individual organic components of interest. Microbial OM, a significant constituent of labile OM pool, is determined through chloroform fumigation. Generally, the refractory OM fraction stabilized by humification processes is defined as humic substance. This OM fraction can be further divided into three subfractions, fulvic acid, humic acid and humin, according to their solubility in alkali (e.g. NaOH and tetrasodium pyrophosphate ($Na_4P_2O_7$)) and acid (e.g. HCl and H_2SO_4) (Giovanela et al., 2010). For instance, Na^+ from NaOH substitutes for H^+-bridges within OM, and consequently, the free OM with relatively high molecular weight is extracted (Schnitzer and Schuppli, 1989). By contrast, complex OM associating with minerals via polyvalent cation bridges is removed by $Na_4P_2O_7$ (Belzile et al., 1997; Prentice and Webb, 2010; Santín et al., 2009).

Fractions being isolated by various chemical fractionation methods remain contrary in terms of degradation degree, and the properties of these fractions depend largely on soil and sediment types. Overall, these fractionation procedures still extract heterogeneous OM pools, because OM pools which are stabilized by different mechanisms might be resolved in the same agent. Therefore, new fractionation procedures have to be developed for the understanding of OM stabilization processes, and particularly for the differentiation between the refractory nature of OM and the other preservation mechanisms.

1.6.3 Consecutive fractionation

Despite a wide range of physical and chemical OM fractionation methods have been developed, almost none of a single fractionation procedure so far is able to isolate OM fractions that are homogenous in stabilization mechanism or turnover time. Therefore, stepwise fractionation approaches have been established for elucidating different mechanisms involved in OM stabilization. A classical approach is a combination of physical and chemical fractionation methods, which can be well exemplified by a density or particle size fractionation followed by a solvent extraction (Jagadamma and Lal, 2010; Leifeld and Kögel-Knabner, 2001). This combined fractionation method provides a moderate contribution to the understanding of the stabilization mechanisms, since information of spatial arrangement and molecular interactions can be obtained simultaneously. Nonetheless, the isolated OM fractions still consist of more than one functional group and the key processes remain unclear.

As previously discussed (Section 1.6.2), hot water extraction removes microbial carbohydrates and N-containing compounds with high bioavailability. Hydrolysis with HCl removes similar biomacromolecular components with hot water extraction but of higher extraction efficiency and intensity. Therefore, the isolated proteins, nucleic acids, carbohydrates and carboxylic have higher stability than those isolated from hot water extraction. H_2O_2 oxidizable OM contains more aromatic compounds, and $Na_2S_2O_8$ oxidizes more aliphatic compounds from bulk samples.

A sequential fractionation protocol which extracts sedimentary OM with hot water, HCl, H_2O_2 and $Na_2S_2O_8$ in sequence was established in this thesis. The sequence of these four steps was arranged in order to yield OM residues with increasing recalcitrance. In fact, chemical fractionation has rarely been conducted on sediments, but it is worth to be introduced to sediment core studies due to the distinctions of biomacromolecular composition and degradation environment between soils and sediments. Instead of tracing the cycling of OM through an individual organic compound, this procedure studied the OM degradation processes by determining down-core variations of the biogeochemical proxies in the isolated fractions. Nowadays, these OM fractions can be better defined, since more advanced analytical techniques have been applied to characterize OM in the past years. Techniques, such as solid-state nuclear magnetic resonance (NMR) spectroscopy, pyrolysis gas chromatography-mass spectrometry

(Py-GC/MS), elemental analyzer-isotope ratio mass spectrometry (EA-IRMS), and Fourier transform infrared spectroscopy (FTIR), are extensively used to gain molecular and structural information about sedimentary OM (Alderson et al., 2016; Chen and Hur, 2015; Mylotte et al., 2014).

1.7 Objectives of thesis

The primary objectives of this thesis include (1) the establishment of a sequential chemical fractionation procedure to obtain sedimentary OM fractions with distinguishable biomacromolecular and isotopic compositions, (2) the identification of terrestrial and aquatic sources in sinking POM and sediment cores, (3) the analysis of the correlation between stable isotopic compositions and biomacromolecular compositions of sedimentary OM, as well as its feasibility for sediment core studies and (4) a systematic interpretation of the OM accumulation and degradation patterns in lake sediments.

Special focus was placed on how land use in the catchment and basin topography affect the proportions of terrestrial and aquatic sources in sinking POM and sedimentary OM, and how these two factors alter the biogeochemistry of OM in sediments.

This thesis consists of three parts, which are:

i. The development of a hydrolysis and wet oxidation combined fractionation method and the characterization of residual fractions by solid-state ^{13}C-NMR analysis and EA-IRMS along with the isotopic measure of the extracts.
ii. Elemental and isotopic analyses of suspended POM, sinking POM and sedimentary OM at the deep and shallow sites in two pre-dams which are contrasting in land use of their catchments.
iii. Employment of the sequential fractionation procedure in sediment core studies to obtain vertical degradation profiles with regard to the biomacromolecular compositions of sedimentary OM as well as the degradability of each organic component.

Chapter 2 Study site and methods

This chapter focuses on the basic aspects of sampling, sample treatments, the analytical techniques as well as data analysis, namely, all the materials, devices, methods and calculations involved in this work. Section 2.1 gives a detailed description of the sampling sites, including location, hydrology, geology, land use in the catchment area. Section 2.2 describes the sampling of POM from the water column and sediments. Section 2.3 detailed the protocol of the sequential chemical fractionation used for the separation of sedimentary OM. Section 2.4 and 2.5 introduces the characterization of POM with EA-IRMS and solid-state ^{13}C-NMR spectroscopy and the statistical analysis of data.

2.1 Site description

The study site was Rappbode Reservoir System (RRS) that locates in Harz region, state of Saxony-Anhalt, Germany (**Fig. 2.1**). RRS is the largest drinking water supplying system in Germany with a total storage capacity of 113.4 Mio m^3. It is comprised of a main reservoir (Rappbode reservoir) and five auxiliary reservoirs, of which two auxiliary reservoirs, Königshütte diversionary dam and Mandelholz dam, are flood control barriers, and the downstream Wendefurth dam is used for hydroelectricity production. The other two dams, Hassel and Rappbode pre-dams, were constructed at the upstream of the main reservoir in the beginning of 1960's. They were closed for reconstruction in 2014 and 2013, respectively. The water volume of pre-dam is normally regulated by the spillway, while the outlet designed at the bottom of the pre-dam is only used under extreme hydrological situations. The foremost role of pre-dam is sedimentation basin, which is constructed to reduce the particles flowing into the main reservoir and avoid siltation. Later on, due to the extensive anthropogenic activities in the catchment and consequently increasing nutrient loads in the reservoir, these two pre-dams play another important role which is for nutrient elimination. The retention of nutrients activates the primary production and thus may give rise to the high sedimentation rates in pre-dams.

Hassel and Rappbode pre-dams, which are the sampling sites in this dissertation, are morphologically alike and share similarities in hydrology and geology such as water surface area, water storage capacity and catchment size (**Table 2.1**). However, due to the precipitation

gradient from North-West to South-West, the annual precipitation in Rappbode pre-dam catchment ranges from 900 mm to 1,200 mm, while it is 100-200 mm lower in Hassel pre-dam catchment (Friese et al., 2014). Moreover, land use in the catchments of both pre-dams is largely differentiated. The catchment of Rappbode pre-dam is predominantly covered with forest (72%) and grassland (22%), and only about 2% of the catchment is utilized for agriculture. By contrast, agricultural land constitutes one-quarter of the catchment area of Hassel pre-dam, whereas forest and grassland constitute 37% and 33%, respectively (**Fig. 2.1**). These disparities in land use imply also the catchments of two pre-dams are dissimilar in soil type. Particularly, grassland is dominated by a mixture of nutrient-depleted gleysols and cambisols. However, agricultural land consists mainly of cambisols which are relatively richer in nutrients and have greater cation exchange capacities. It influences thereby the biomacromolecular compositions and retention times of detritus in the catchment and then the inputs to the pre-dams.

Table 2.1 Morphometric, hydrological and chemical characteristics of Hassel and Rappbode pre-dam

Parameters	Rappbode pre-dam	Hassel pre-dam	References
Surface area (km^2)	0.218	0.288	Rinke et al. (2013)
Catchment area (km^2)	47.6	44.6	Friese et al. (2014)
Capacity (10^6 m^3)	1.66	1.64	Friese et al. (2014), Wendt-Potthoff et al. (2014)
Water retention time (day)[a]	51.7	65.2	Friese et al. (2014)
Annual inflow (10^6 m^3)[b]	29.0	19.4	Friese et al. (2014), Tittel et al. (2015)
Maximum water depth (m)	17	14	Friese et al. (2014)
pH	6.5-8.4	6.5-9.6	Dadi (2016)
Total P (mg L^{-1})[c]	0.013	0.019	Wendt-Potthoff et al. (2014)
SRP (mg L^{-1})[c]	0.004	0.007	Wendt-Potthoff et al. (2014)
NO_3^--N (mg L^{-1})[c]	0.81	3.00	Wendt-Potthoff et al. (2014)
NH_4^+-N (mg L^{-1})[c]	0.05	0.11	Wendt-Potthoff et al. (2014)

[a] Medians of the monitoring data of 137 days in Rappbode pre-dam and 317 days in Hassel pre-dam.
[b] Medians of data collected from1998 to 2011 in Rappbode and Hassel pre-dams.
[c] Concentrations of nutrients in Rappbode and Hassel pre-dams which measured on March 30, 2011.

Even though the water quality and stratification do not differ considerably between two pre-dams, the nutrient loads in particular nitrate and phosphorous concentrations are prominently

higher in Hassel pre-dam (**Table 2.1**), and the concentration of dissolved organic carbon is higher in Rappbode pre-dam. The water retention time is on average 13 days longer for Hassel pre-dam. As a consequence, Hassel pre-dam is eutrophic and dominated by cyanobacteria in summer, while Rappbode pre-dam is mesotrophic and dominated by diatoms (Friese et al., 2014). Apart from the distinction regarding phytoplankton community in the water column, microbial biomass in sediments is usually two times higher in Hassel pre-dam. For these reasons, the biochemical structures and degradation processes of POM in these two pre-dams are supposed to be different. Within each pre-dam, the stratification occurs in the water column and the sedimentation processes are distinct among sampling sites with different water depths. On account of the construction of pre-dams, shallow sites are geographically closer to the inflows (**Fig. 2.1**) and have thus higher sedimentation rates (Dadi et al., 2016). For a comprehensive comparison, hence, sediments were collected from both the shallow site (with a water depth of 4 m in Rappbode pre-dam and also in Hassel pre-dam) and the deep site (17 m in Rappbode pre-dam and 14 m in Hassel pre-dam).

2.2 Sampling of particulate organic matter

2.2.1 Sampling of suspended particulate organic matter

Suspended POM was sampled on September 16th, 2016 in Hassel and Rappbode pre-dams. To be specific, two control water samples with a volume of 20 L were collected from epilimnion at the deep site of each pre-dam (YH3, 51.709°N, 10.832 °E in Hassel and YR3, 51.709°N, 10.798°E in Rappbode, **Fig. 2.1**). Suspended material was separated from bulk water samples via ultrafiltration with a cassette which the pore size is 0.45 µm. About 19 L water passed through the ultrafiltration system, and the remained 1 L concentrated water was centrifuged at 10,000 rpm for 15 min (Beckman Coulter J2-MC High Speed Centrifuge, Minnesota, United States of America). The residue was placed in an evaporated dish and dried in an oven at 45 ˚C. The obtained suspended material was then ground for the characterization of suspended POM.

Suspended POM in this work is considered that mainly consist of algae. This is based on the findings of Friese et al. (2014) who has collected suspended POM with an identical filtration way in the same two pre-dams. Furthermore, similar observations have been reported in other aquatic

systems with regard to the dominance of algae in suspended POM (Engel and Macko, 2013; Nebbioso and Piccolo, 2013; Smetacek and Hendrikson, 1979).

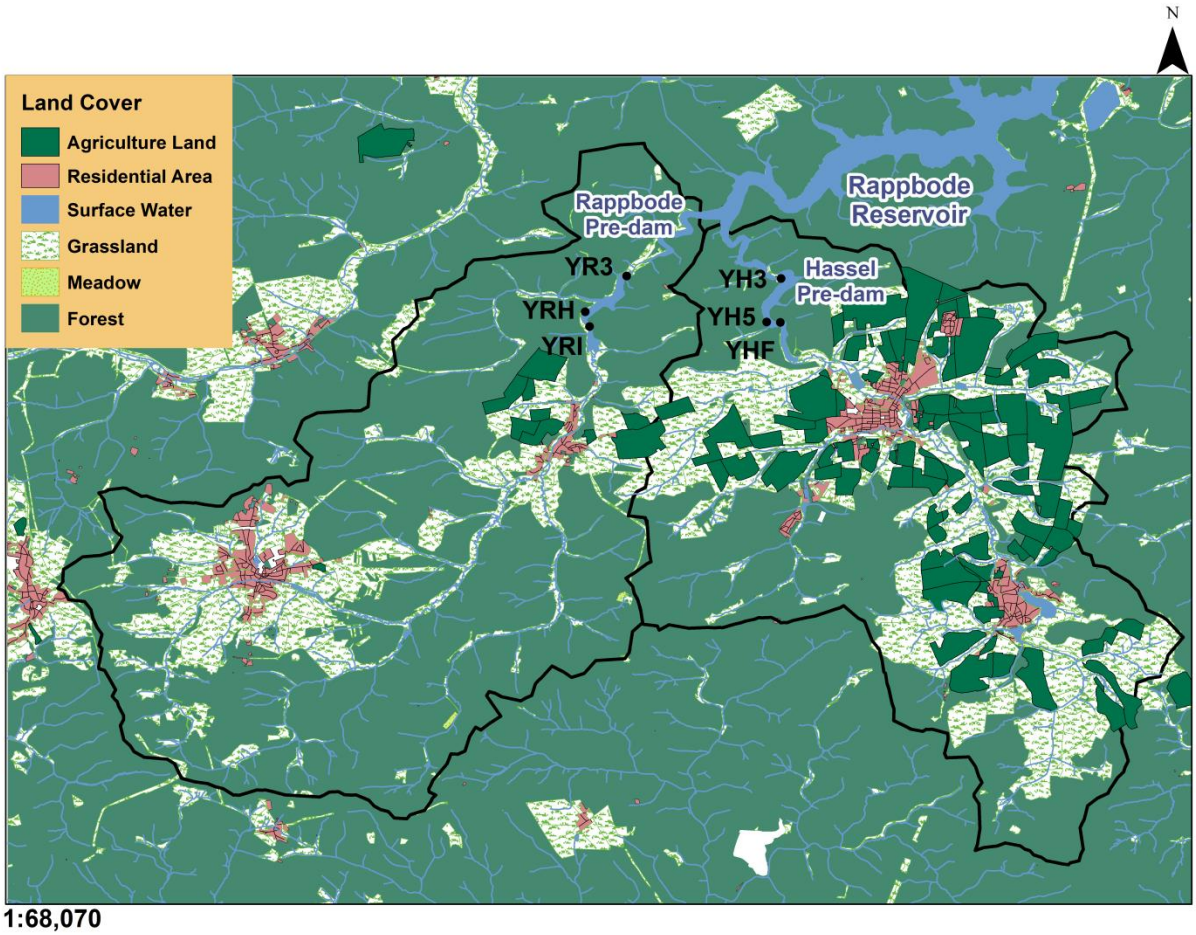


Fig. 2.1 Rappbode and Hassel pre-dams in Rappbode Reservoir System along with the land use in the catchments (Data were provided by ATKIS1 DGM50 M745; Geobasisdaten© Vermessungsverwaltungen der Bundesländer und BKG (www.bkg.bund.de); Map was created by ArcGIS). Black solid dots were sediment sampling sites, of which YR3 and YH3 located at the deep sites, and YRI and YHF located at the shallow near inflow sites of pre-dams.

2.2.2 Sampling of sinking particulate organic matter

Sinking POM was sampled from Hassel and Rappbode pre-dams monthly with sediment traps in 2016. Sediment traps did not work during the frozen season, so samples in January, February (at the shallow and deep sites) and December (at only the shallow site) were not available. Besides, few samples were lost by accident. Sediment traps are designed originally to measure the depositional flux of POM at a given water depth, and the collection time depends largely on the sedimentation rate and turbulent intensity in water basin (Baker et al., 1988;

FLEMING et al., 1979). The sediment trap used in this work consists of one polyvinyl chloride (PVC) pipe and two Plexiglas cylindrical tubes (diameter of 86 mm) which were immobilized at both sides of the sturdy pipe. To immobilize the sampling point of sinking POM, the terminal of sediment trap was connected to a gravity anchor.

At the deep site of Hassel pre-dam (YH3) sediments traps were deployed at two depths, whereas only one sediment trap was allocated at the shallow site (YH5, 51.703°N, 10.829 °E, **Fig. 2.1**). Similarly, in Rappbode pre-dam, two sediment traps (**Fig. 2.2** Simplified profiles of Rappbode and Hassel pre-dams. Sediment depth marked with n=3 means three replicates were taken from these sediment layer for OM fractionation. Sediment depth marked with ^{13}C NMR means that sediments sampled at this depth were analyzed with EA-IRMS and solid-state ^{13}C NMR spectroscopy, while the remained depths were merely analyzed with EA-IRMS.) were deployed at the deep site (YR3) and one sediment trap was installed at the shallow site (YRH, 51.704°N, 10.789°E, **Fig. 2.1**). The collected samples were left in the laboratory for 1 to 2 days until the absolutely settling down of the suspended POM. Afterwards, the supernatant was separated carefully from the settled POM via pouring. The rest mixture of the supernatant and residue was centrifuged at 3,500 rpm, 8 ˚C for 15 min (Heraeus Labofuge 400R, Heraeus Quarzglas GmbH & Co. KG, Bitterfeld-Wolfen, Germany), and the supernatant was discarded. The sedimentary residue was freeze-dried and ground with agate mortar for elemental and isotopic determinations.

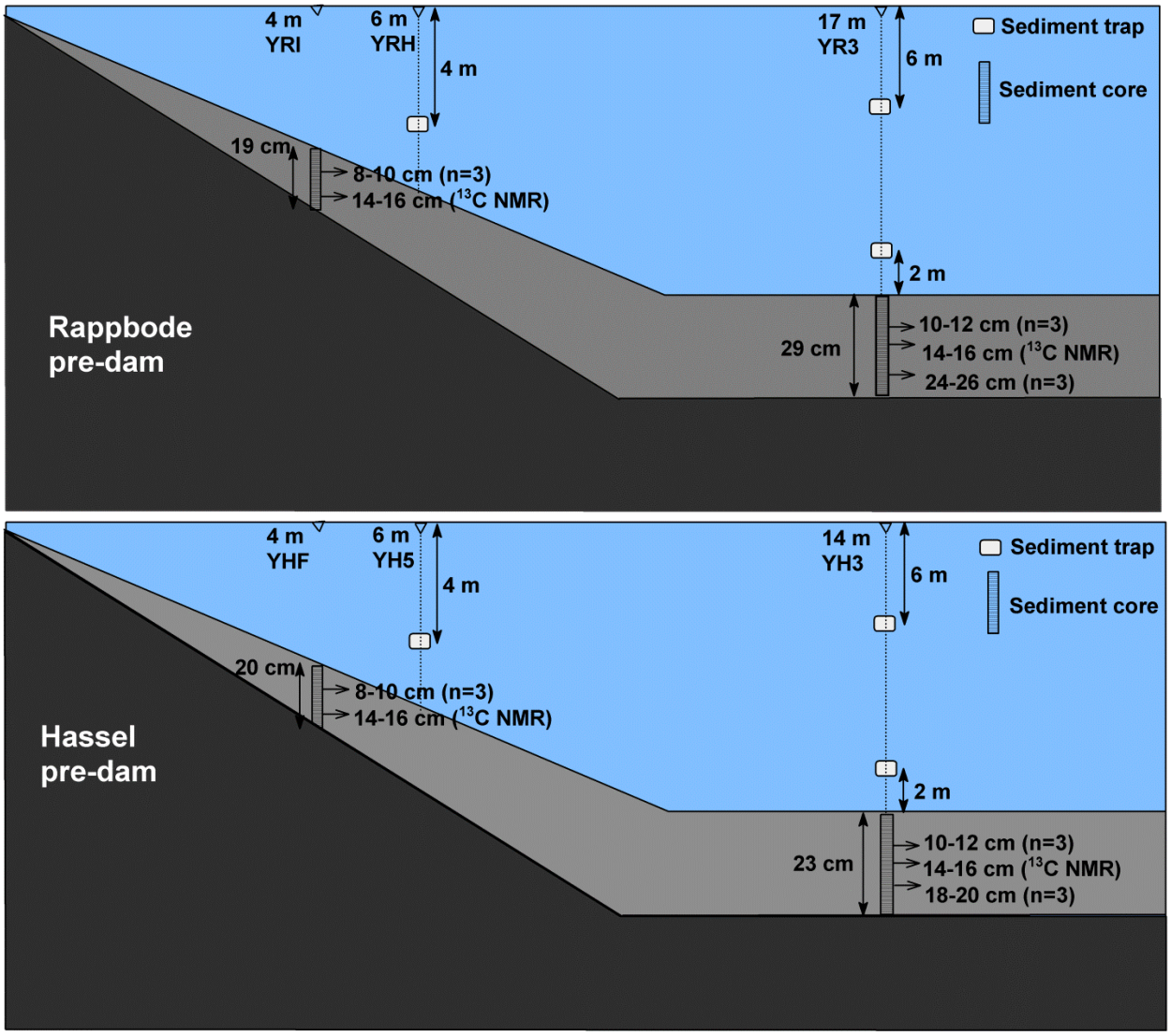


Fig. 2.2 Simplified profiles of Rappbode and Hassel pre-dams. Sediment depth marked with n=3 means three replicates were taken from these sediment layer for OM fractionation. Sediment depth marked with ^{13}C NMR means that sediments sampled at this depth were analyzed with EA-IRMS and solid-state ^{13}C NMR spectroscopy, while the remained depths were merely analyzed with EA-IRMS.

2.2.3 Sediment sampling

Sediment samples were collected from the deep sites (YH3 and YR3) and shallow sites (YHF, 51.703°N, 10.832 °E in Hassel and YRI, 51.702°N, 10.790°E in Rappbode, **Fig. 2.1**) of both pre-dams. Sediment cores were taken on April 5 to 6, 2011 from Rappbode pre-dam and on April 12 to 13, 2011 from Hassel pre-dam. Four replicates of sediment core were prepared at each deep and shallow sampling site. Sediment samples were collected by a modified Kajak gravity corer (UWITEC, Austria) equipped with a polyvinyl chloride (PVC) cylindrical tube which was 9 cm

in diameter and 60 cm in length. The PVC tubes were plugged by elastic rubbers with the impulse of falling gravity anchor (Dadi, 2016). Parameters such as pH, temperature and redox property were measured on-site. The PVC tubes were filled with 20-30 cm of undisturbed sediment and the rest of overlying deep water, and then closed with a tight cover to protect the sediment from oxygen and disturbance during the transport. In the laboratory, sediment cores were sliced into layers with a depth of 2 cm for biochemical analyses. The sediment slices were freeze-dried, and large detritus and roots were excluded manually from dry sediments. Samples were ground into fine powder with agate mortar and pestle, which was critical for the following measures.

The material used for the test of the fractionation method was a mixture of surface sediments that collected with a grab sampler from different sampling sites in Hassel pre-dam. Sediment used for fractionation method test was named ‘reference material’.

2.3 Sequential chemical fractionation of sedimentary organic matter

A simplified procedure of the stepwise fractionation was given in **Fig. 2.3**. The fractionation procedure was started with hot water extraction which was partly derived from the method of Ghani et al. (2003) and Leinweber et al. (1995). In this work, a weight of 3 g homogeneous sediments (6 replicates) was taken into a polypropylene centrifuge tube and dispersed in 30 mL Milli-Q water by the ultrasonic bath (200 rpm, room temperature and 30 min). Suspensions were then centrifuged (3,500 rpm, 20 ˚C and 20 min), and the supernatant was discarded after wiping the large detritus out with a spatula. Another 30 mL of Milli-Q water was added into a centrifuge tube with residue, and the closed tube was mixed with vortex shaker (Multifunction Vortex Mixer Set VM-10, witeg Labortechnik GmbH, Wertheim, Germany) for 15 s. Sediments and water reacted in a water-bath at 80 ˚C for 24 h. In the end of extraction with hot water, the centrifuge tube was shaken with vortex shaker for 60 s with proper speed in order to achieve the absolute release of hot water extractable OM. The reacted suspension was centrifuged (3,500 rpm, 20 ˚C and 20 min), and the supernatant passed through 0.45 µm cellulose nitrate membrane filters. The filtrate was collected for analysis, and the filter residue was combined with centrifuge residue and dried in an oven (Umluft-Trockenschrank, 53L, 300°C, Heraeus UT 6060, Heraeus Quarzglas GmbH & Co. KG, Bitterfeld-Wolfen, Germany) at the temperature of

60 ˚C. The dried treated sediment was homogenized with an agate mortar and kept in a vacuum desiccator for characterization and extraction with acid.

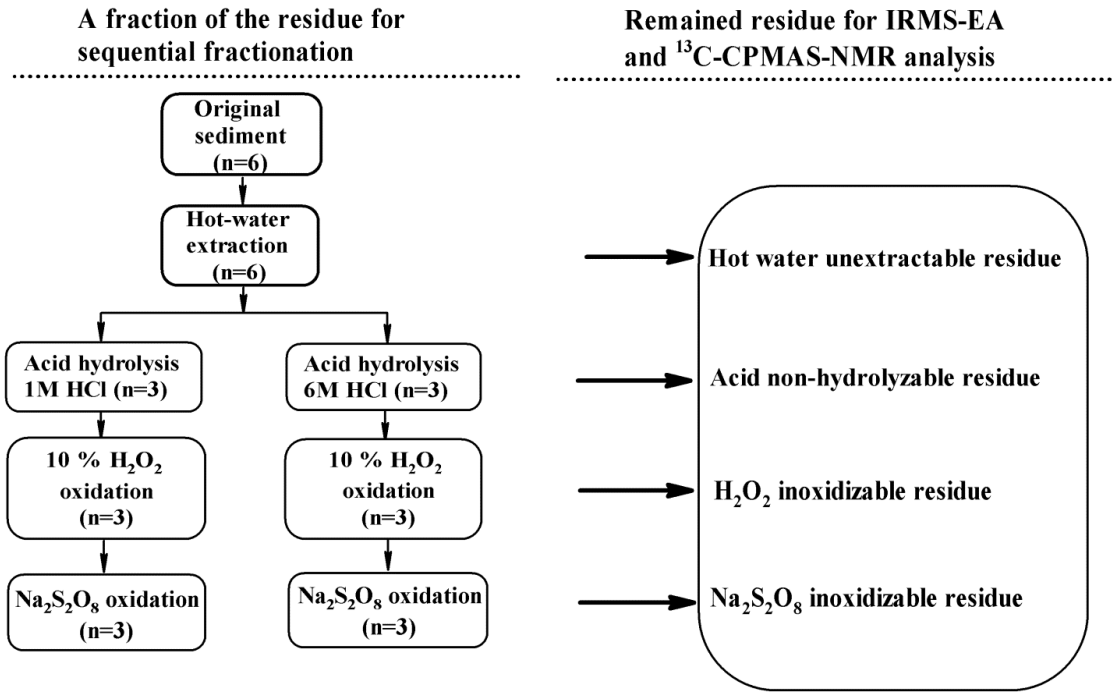


Fig. 2.3 Simplified scheme of sequential fractionation procedure. The fractionation was started with six replicates and extracted with hot water, then three of replicates were treated with 1 M HCl and the left three replicates treated with 6 M HCl. Both groups of three replicates were oxidized by 10% H_2O_2 and $Na_2S_2O_8$, successively. After one fractionation step, a portion of sediment residue was collected for determination and the other portion proceeded for further fractionation until the procedure finished.

To attest the effect of acid concentration on the extraction efficiency of acid hydrolysis, half of the hot water-treated sediment replicates were further hydrolyzed by 6 M HCl and the left half of replicates were hydrolyzed by 1 M HCl. Briefly, 2 g of hot water-treated sediments were hydrolyzed with 25 mL 1 M or 6 M HCl in a water bath at 80 ˚C (Silveira et al., 2008) after well mixed by an oscillator (TitroWiCo Orbital Shaker, Bochum, Germany) for approximate 2 h. The reaction lasted for 20 h. HCl-hydrolyzed OM was separated from the resistant residue by centrifugation (3,000 rpm, 20 ºC and 15 min). The supernatant containing hydrolyzed OM was collected for characterization, and the HCl resistant residue was washed with 5 mL Milli-Q water and repeated for three times. When HCl resistant residue was separated by centrifugation (3,500 rpm, 20 ºC and 10 min), and the washings were merged into supernatant containing hydrolyzed OM. The centrifugation residue was collected by spatula from the centrifuge tube and transferred

to a glass evaporating dish for drying. Humid sediments were dried at 60 ˚C in the oven and ground into fine powder with an agate mortar and pestle for further analyses and fractionation.

After the extractions with hot water and HCl (1 M and 6 M), sediments were continuously oxidized by H_2O_2. The procedure deployed in this work was largely based on the methods of soil OM fractionation from Jagadamma et al. (2009) and Helfrich et al. (2007). It was a multi-step process that began with the dispersion of 1 g HCl-resistant sediment into 10 mL Milli-Q water. Two doses of 10 mL 10% H_2O_2 were added into the suspension with a time interval of 3 h. Within this 3 h, centrifuge tube was kept shaking in an ultrasonic bath for the adequate reaction of reactants. After the second addition of H_2O_2, centrifuge tubes were placed in a water bath (50 ˚C without shaking) and stayed overnight. The last dose of H_2O_2 was then added and reacted for another one to two days until the mixture of sediment and solution stopped effervescing. Centrifuge tubes were thoroughly shaken by vortex shaker for 60 s and reacted for 2 h to avoid any retained H_2O_2-oxidizable OM in the solid phase. By centrifuging the mixture (3,000 rpm, 20 ºC and 20 min), the supernatant was separated and collected. The residue was washed by 10 mL 10% H_2O_2 centrifuged (3,000 rpm, 20 ºC and 20 min) and followed by repeated washing with 5 mL Milli-Q water for three times. The washings were combined with the supernatant. The H_2O_2 resistant residue was dried at a relatively low temperature (45 ºC) and finally homogenized with agate mortar and pestle. The fine H_2O_2 resistant residue was saved in a vacuum desiccator for analyses.

Following the treatment with H_2O_2, the homogenized residue was exposed to $Na_2S_2O_8$ oxidation. To be specific, H_2O_2 resistant sediments (0.5 g) were dispersed in 40 mL Milli-Q water, leaving in an ultrasonic bath for 20 min. Later on, the suspension in centrifuge tube was reacted with 4 g of $Na_2S_2O_8$, and the reaction was buffered with 4.4 g $NaHCO_3$ (Helfrich et al., 2007; Lorenz et al., 2008). Before the centrifuge tube was placed into a water bath, fine sediments and chemical reagents had to be mixed well with vortex shaker. The reaction was taken placed at 80 ºC and went on for 18 to 24 h until effervescing ceased. After the reaction finished, centrifuge tube was disturbed with vortex shaker and centrifuged at 3,500 rpm, 20 ºC for 20 min. The supernatant was collected, and the residue was washed with 10 mL Milli-Q water for three times, and likewise, washings were separated by centrifuging (3,500 rpm, 20 ºC and 10 min). As a small fraction of carbonate was assumed to remain in humid sediments,

sediments were first dried and homogenized by grinding and then acidized with 20 mL 1 M HCl. Reactions lasted for 18 h with moderate shaking (180 rpm, 25 ºC). For isolating the residue, the suspension was re-centrifuged at 3,500 rpm, 20 ºC for 20 min. The final residue was washed with Milli-Q water until it was neutral. It was dried at a mild temperature (40 ºC) and homogenized with an agate mortar and pestle for isotopic and ^{13}C NMR analyses.

In sediment core study, three sediment replicates were taken, from depths of 10-12 cm and 18-20 cm at the deep site and 8-10 cm at the shallow site in Hassel pre-dam, and depths 10-12 cm and 24-26 cm at the deep site and 8-10 cm at the shallow site in Rappbode pre-dam, for the sequential fractionation of sedimentary OM (**Fig. 2.2**).

2.4 Geochemical analyses

For the clarification of POM alterations during the sinking, deposition and diagenesis, total organic carbon, total nitrogen and stable carbon and nitrogen isotopic compositions were determined by EA-IRMS (for details see 2.4.1). Measures carried out on the bulk samples collected from the water column, sediment traps and sediment cores and also on the isolated chemical fractions. Chemical resistant fractions were particularly analyzed by solid-state ^{13}C NMR (for details see 2.4.3), which shed light on the variations of biomacromolecular composition along the fractionation procedure. Furthermore, HCl and H_2O_2 resistant sediments (with sediment depth of 14-16 cm, **Fig. 2.2**) sampled from the deep and shallow sites of both pre-dams were also analyzed by solid-state ^{13}C NMR spectroscopy to assist the interpretation of the results derived from EA-IRMS measures.

2.4.1 C/N ratios and stable isotopic compositions in residues

Equipment used in this work was Flash 2000 EA coupled with DELTA V advantage IRMS (Thermo Fisher Scientific, Bremen, Germany, analyzed by Ines Locker from Central Laboratory for Water Analytics & Chemometrics, Helmholtz Centre for Environmental Research, Magdeburg, Germany) with an external precision of 1% for carbon, 1% for nitrogen, 0.008‰ for C isotopic composition and 0.15‰ for N isotopic composition, respectively. Due to the limit of detection, the weights of tested samples had to be adjusted for bulk sediments and various chemical resistant residues. Of which, 4 milligrams of bulk samples, whereas 5 milligrams of hot

water and HCl resistant sediments, 20 milligrams of H_2O_2 and $Na_2S_2O_8$ resistant were used to achieve sufficient signals in EA-IRMS analysis.

Samples were weighed into tin capsules, and bulk samples were pre-treated with a drop of 0.1 M HCl before the measurements to exclude the inorganic carbon. Residual HCl was removed by evaporating in an oven at 60 ºC, then the capsules were closed and crimpled for measurement. Capsules were placed in EA and sequentially combusted into purified gases (CO_2, N_2, H_2, SO_2, etc.) in a furnace at a temperature up to 1020 ºC (Brodie et al., 2011). CO_2 and N_2 were dashed by helium to a thermal conductivity sensor, and accordingly, the contents of C and N were measured as percentages (wt.%). Then these percentages were converted into absolute C and N masses in one gram of dry sediment in this work (mg g^{-1}). C/N ratio was calculated as follows:

$$\frac{C}{N} ratio = \frac{\text{C content}}{\text{N content}} \times 1.167 \quad (1)$$

where the constant of 1.167 is the ratio of atomic weights of nitrogen and carbon. The gases were passed forward to IRMS, and the isotopic compositions were obtained by comparing the tested gases with standard materials (Vienna Pee Dee Belemnite for $\delta^{13}C$ and atmosphere N_2 for $\delta^{15}N$) as the following Equation:

$$\delta(‰) = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000 \quad (2)$$

where, δ represents the value of stable isotope ratio, and R_{sample} and $R_{standard}$ represent the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ ratios of tested samples and standard materials, respectively (Coplen et al., 2006; Kayler et al., 2011). Stable isotope ratio was given in per mil (‰).

2.4.2 C concentration and stable carbon isotope ratio in solutions

OM fractions dissolved in chemical solutions during fractionation were measured in the Department of Geography and Geosciences, GeoCentre Nordbayern, Friedrich-Alexander University in Erlangen, Germany. The determinations of C concentration and $\delta^{13}C$ value were performed by EA-IRMS (Thermo Fisher Delta V Plus, Bremen, Germany) that coupled with a continuous flow mode Optical Instruments Analytical Aurora 1030W TOC analyzer (College

Station, Texas, USA). The external precision for OC in solution was 0.03 mmol L^{-1}. The $\delta^{13}C$ value was calculated as Equation (2) in section 2.4.

2.4.3 Structural characterization of organic matter

Structural characterization of sedimentary OM was accomplished by Bruker Avance 300 NMR spectroscopy (Bruker Biospin, Bremen, Germany) operating at a ^{13}C frequency of 75.47 MHz which linked to BL-4 Cross Polarization/ Magic Angle Spinning (CP/MAS) probe head at the Institute of Chemistry from the Otto von Guericke University of Magdeburg. Sediments were packed into 4 mm ZrO_2 rotors. The analysis was performed by setting the proton 90° pulse as 3.3 µs, the acquisition decoupling strength as 69 kHz. Other parameters like spinning rate was 5 kHz (fractions obtained from 'reference material') or 15 kHz (fractions isolated in sediment core studies), recycle delay was 2-3 s, contact time was 2 ms.

Chemical shifts assignment was externally referenced to the glycine resonance at 176.03 ppm, and the spectra were recorded with a width of 350 ppm. To calculate the intensity of a defined functional group, integrations of ^{13}C NMR spectra were primary referred to the definitions of Gélinas et al. (2001), Rodríguez-Murillo et al. (2011) and Pane et al. (2013). Accordingly, alkyl compounds, N-alkyl-methoxy compounds, O/O_2-alkyl compounds and acetals, aromatic compounds, O-aromatic structures with phenols, esters together with carboxyl or carbonyl compounds were assumed to be resonated at -10-45 ppm, 45-60 ppm, 60-95 ppm, 95-110 ppm, 110-145 ppm, 145-160 ppm, and 160-210 ppm, respectively. By correcting the baseline and resonance phases and integrating the chemical shifts, the relative abundance of various functional groups was calculated.

Alkyl compounds were predominately characterized by waxes, steroids, tannins, cutans, and N and O/O_2 substituted alkyl compounds comprised a small portion of total OM and encompassed of proteins, carbohydrates, alcohols, fatty acids. Typical aromatic compounds in sediments were lignins and lignin-like products but also some lipids and double bonds from triacylglyceride (TAG). Signals of amides, esters, ketones, aliphatic acids, benzene carboxylic acids were more often occurred in the carboxylic resonating region (Maksymowska et al., 2000; Rodríguez-Murillo et al., 2011). To assess the biomacromolecular structure of sedimentary OM, these organic compounds were simplified into six model components, which were carbohydrates,

proteins, lignins, lipids, carbonyls and char. Therefore a mixing model described by Baldock et al. (2004) and Nelson and Baldock (2005) was applied to calculate the proportions of different model components. In order to obtain a better agreement between actual and predicted distributions of signal intensity in ^{13}C NMR spectral regions, a 'Terrestrial' model (Nelson and Baldock, 2005) was selected (**Table 2.2**).

Table 2.2 Distribution of OC in chemical shift regions of ^{13}C NMR spectra and the representative atomic C/N for six basic components. After Nelson and Baldock (2005)

Spectral region (ppm)	Carbohydrates (%)	Proteins [a] (%)	Lignins (%)	Lipids [a] (%)	Carbonyls (%)	Chars (%)
-10-45	0.0	39.6	10.5	75.6	0.0	5.6
45-60	4.3	21.9	13.8	4.5	0.0	0.0
60-95	79.0	2.1	12.5	9.0	0.0	0.0
95-110	15.7	0.0	8.6	0.0	0.0	4.3
110-145	1.0	7.5	30.6	3.6	0.0	73.9
145-165	0.0	2.5	19.5	0.7	0.0	16.1
165-210	0.0	26.4	4.6	6.6	100.0	5.6
Atomic N/C	0.00	0.32	0.00	0.00	0.00	0.00

[a] Organic components with different distributions of OC in aquatic and terrestrial systems, but the terrestrial system was chosen in this table.

The biomacromolecular composition (in percentage) was calculated by solving Equations (3) to (8) (Nelson and Baldock, 2005).

$$A + B + C + D + E + F = 100 \quad (3)$$

$$m_a A + m_b B + m_c C + m_d D + m_e E + m_f F = m_{sample} \quad (4)$$

$$\alpha_a A + \alpha_b B + \alpha_c C + \alpha_d D + \alpha_e E + \alpha_f F = \alpha_{sample} \quad (5)$$

$$\beta_a A + \beta_b B + \beta_c C + \beta_d D + \beta_e E + \beta_f F = \beta_{sample} \quad (6)$$

$$\gamma_a A + \gamma_b B + \gamma_c C + \gamma_d D + \gamma_e E + \gamma_f F = \gamma_{sample} \quad (7)$$

$$\varepsilon_a A + \varepsilon_b B + \varepsilon_c C + \varepsilon_d D + \varepsilon_e E + \varepsilon_f F = \varepsilon_{sample} \quad (8)$$

Where, A, B, C, D, E, F are the proportions of carbohydrate, protein, lignin, lipid, carbonyl and char, respectively. In Equations (3) to (8), m_i, α_i, β_i, γ_i, ε_i (i=a, b, c, d, e, f, sample) equal the C/N ratio and the proportions of carbon distribute in the chemical shift regions of -10-45 ppm, 60-95 ppm, 210-165 ppm and 110-145 ppm, respectively, of which, the subscribe 'i' represents the sub-proportions in six model components and the ratio or proportions in the measured sample.

2.5 Statistical analyses

The efficiency of the developed sediment fractionation procedure was assessed by the reduction of C and N contents and stable isotope ratio shifts between two extraction steps. C and N contents, $\delta^{13}C$ and $\delta^{15}N$ values were compared between untreated sediments and hot water unextractable residue, hot water unextractable residue and HCl nonhydrolyzable residue, HCl nonhydrolyzable residue and H_2O_2 resistant residue, H_2O_2 and $Na_2S_2O_8$ resistant residues. Specifically, the determined values of the former fractionation residue were subtracted from the corresponding values of the later fractionation residue. All measuring results were given in mean ± standard deviation.

In sediment core study, mean values and standard deviations of elemental contents and stable isotopic compositions were only calculated on samples with replicates (**Fig. 2.2**). An examination on the precision of fractionation procedure was done by evaluating the coefficients of variance (CV) which were the quotients of standard deviations divided by the corresponding mean value. These CV values were deployed to the whole sediment core to calculate standard deviations for the sediment samples without replicates. Removal of OM caused by each fractionation step was represented by the difference of C or N content between two fractionation steps. In addition, the degradation of sedimentary OM was represented by the vertical variations of C and N contents in sediments.

All comparisons were performed by two-tailed Student's t-test using R (RCore, 2013). In particular, comparisons of the elemental and isotopic compositions between two connected fractionation steps, as well as comparisons between two pre-dams, deep and shallow sites were accomplished by paired t-test. As for the efficiencies of 1 M HCl and 6 M HCl in acid hydrolysis, they were compared with an unpaired t-test. The statistically significant level was fixed as 0.05, but higher significances (p <0.01, p <0.005 or p <0.001) were also given.

Pearson correlation analyses were adopted by using R to evaluate the correlations between C/N ratio and stable isotope ratios. A *P* value less than 0.05 indicated significant correlations. In sediment core study, the trends of C, N contents and stable carbon and nitrogen isotope ratios changing with depth were evaluated by polynomial regressions by using R. Alike to the other statistical analyses, the significant level for polynomial regression analyses was fixed as 0.05. The seasonal trend of elemental and stable isotopic compositions was tested by Seasonal Mann-Kendall test. It was performed in R, and a *P* value<0.05 was considered statistically significant.

Spectra of ^{13}C NMR analyses were handled with TopSpin 3.5 (Bruker, Biospin). The relative abundance of each functional group or organic biomacromolecular component in sedimentary OM was presented in percentage.

Chapter 3 Results

3.1 Biogeochemistry of suspended and sinking particulate organic matter

3.1.1 Elemental contents in suspended and sediment trap material

C and N contents of suspended material in Rappbode pre-dam were 191 mg g^{-1} and 25 mg g^{-1}, respectively, and these contents almost doubled in Hassel pre-dam (335 mg g^{-1} and 45 mg g^{-1}, respectively, **Fig. 3.1**). Suspended material was compared with sediment trap material which was sampled in the same month (September). Sediment trap material in both pre-dams was more depleted in C and N than suspended material throughout the year. The C and N contents of sediment trap material at the deep site peaked at 154 mg g^{-1} and 19 mg g^{-1} in Rappbode pre-dam and at 230 mg g^{-1} and 32 mg g^{-1} in Hassel pre-dam in 2016 (**Fig. 3.1**). Overall, sediment trap material in Hassel pre-dam was generally richer in C and N than that in Rappbode pre-dam.

In Hassel pre-dam, C and N contents of sediment trap material exhibited obvious seasonal trends (with all $P<0.005$, Seasonal Mann-Kendall test) at the shallow and deep sites, showing a rise from July to September (**Fig. 3.1**). In addition, relatively high C and N contents were observed in winter (November and March) at the shallow site but not at the deep site. C and N contents remained relatively low in spring (March to June), except for an unexpectedly high value in March at the shallow site. Distinct differences regarding elemental contents in sediment trap material were also observed between sediment trap material sampled from the deep and shallow sites and between two sampling water depths at the deep sites. Significantly higher C and N contents (both $P< 0.05$ by Student's t-test) were found in the sediment trap material at the deep site than the shallow site. Material trapped at 6 m below the water surface had less C and N than that trapped at 2 m above the sediments.

The changes of C and N contents in sediment trap material of Rappbode pre-dam followed different patterns over the year than that of Hassel pre-dam. C and N contents in Rappbode pre-dam showed seasonal trends (with all $P< 0.005$, Seasonal Mann-Kendall test). However, only slight increases of C and N contents were observed from summer to late autumn in sediment trap material collected in Rappbode pre-dam, if the extremely low values in June at the sampling depth of 2 m above the sediments of the deep site were excluded (**Fig. 3.1**). The differences

regarding the C and contents between the shallow and deep sites and two sampling water depths of the deep site could not be identified with a Student's t-test (P>0.1).

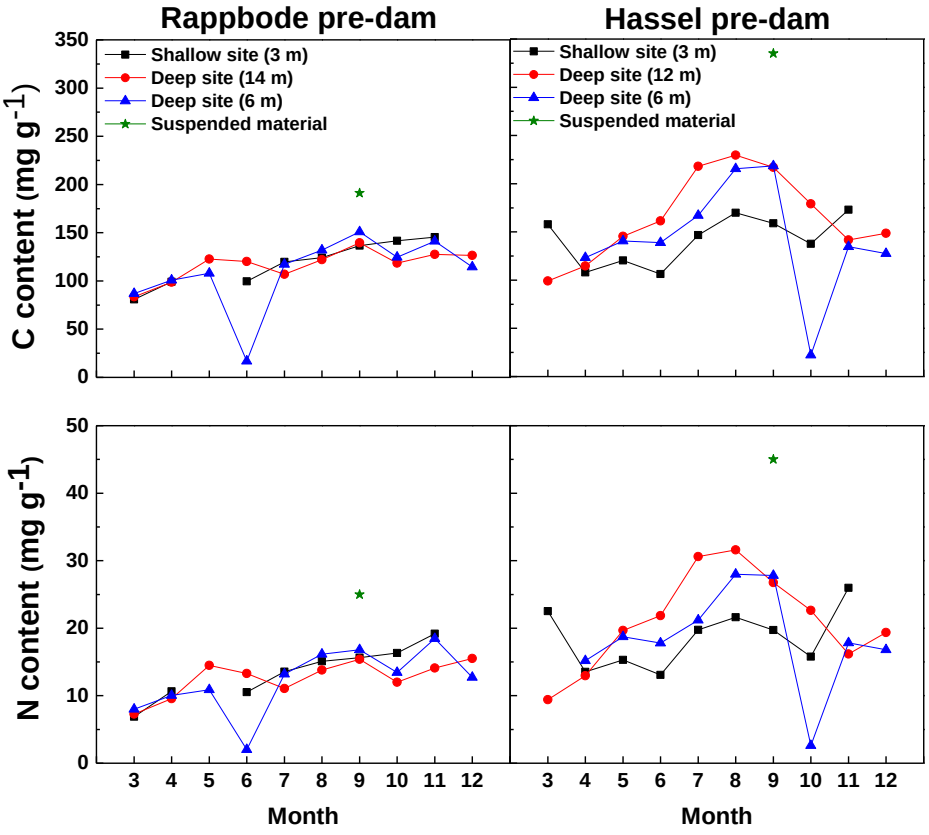


Fig. 3.1 Monthly C and N contents (mg in one gram dry particles) of suspended and sediment trap material in 2016. Black lines with squares represent sinking particles sampled at the shallow sites at a depth of 3 m; blue lines with triangles represent sinking particles sampled at the deep sites 6 m below the water surface; red lines with circles indicate sinking particles sampled at the deep sites 2 m above the sediments; green stars represent suspended material.

3.1.2 Biogeochemical proxies in suspended and sediment trap material

To identify the terrestrial and aquatic sources in POM in the water column, proxies including stable isotope and C/N ratios were determined or calculated. These biogeochemical characteristics of the sediment trap material from Hassel and Rappbode pre-dam were presented in **Fig. 3.2** and **Fig. 3.3**.Suspended POM in Hassel pre-dam had greater C/N (with a difference of 0.5) and $\delta^{13}C$ values (by 0.7‰), compared with the sinking POM sampled from the water depth of 6 m or 14 m at the same site. Similar differences were detected in Rappbode pre-dam (**Fig. 3.2**). In particular, the distinction in $\delta^{13}C$ values between the suspended and sinking POM

was up to 1.8‰. The value of $\delta^{15}N$ was remarkably lower in suspended POM than in sinking POM in Hassel pre-dam with a difference as high as 3‰ (**Fig. 3.3**). However, the $\delta^{15}N$ difference between suspended and sinking POM in Rappbode pre-dam was only 1.4‰ (6 m below the water surface) or even indistinguishable (2 m above the sediments).

Sediment trap material in Rappbode pre-dam had in general greater C/N ratio than material sampled in Hassel pre-dam (**Fig. 3.2**), and the annual average value for three sampling depths (one at the shallow site and the other two at the deep site) was 10.7 for Rappbode and 9.2 for Hassel. In Rappbode pre-dam, C/N ratio of sediment trap material varied apparently with seasons, and the greatest C/N ratio (13.6) was observed in March (**Fig. 3.2**). In Hassel pre-dam, however, C/N ratio was mostly constrained within 10 and had an only modest increase in later autumn (**Fig. 3.2**). Sinking POM (in sediment trap material) in Rappbode was characterized by higher $\delta^{13}C$ values than sinking POM in Hassel pre-dam from spring to early summer as well as in winter (**Fig. 3.2**). A Student's t-test indicated that $\delta^{15}N$ values of sinking POM at three samplings in Hassel pre-dam was significantly higher than in Rappbode pre-dam throughout the year ($P<0.001$). C/N ratio, $\delta^{13}C$ and $\delta^{15}N$ values consistently pointed to a larger proportion of aquatic material in sinking POM in Hassel pre-dam.

Variations of C/N ratio, $\delta^{13}C$ and $\delta^{15}N$ values of sinking POM over the seasons were not consistent in both Hassel and Rappbode pre-dam (**Fig. 3.2** and **Fig. 3.3**). Therefore, higher $\delta^{13}C$ values and C/N ratios occurred in spring in Rappbode pre-dam, whereas higher $\delta^{15}N$ values were observed in autumn. The variation of these biogeochemical proxies in Rappbode pre-dam followed an even more variable pattern. Overall, the enrichment of ^{13}C was found in late spring and autumn. The values of $\delta^{15}N$ decreased in summer and autumn (except the deeper layer at the deep site).

The $\delta^{13}C$ values of sinking POM in Rappbode pre-dam did not differ significantly among different sampling sites ($P>0.05$, Student's t-test). Nevertheless, sinking POM sampled in deeper water depth (2 m above the sediments) at the deep site was characterized by higher C/N ratio but lower $\delta^{15}N$ value than the other two sampling depths. Sinking POM taken from the surface water at the deep site was most enriched in ^{15}N from June to November. In comparison, sinking POM at the shallow site of Hassel pre-dam was generally richer in ^{13}C and ^{15}N and had higher C/N ratio relative to POM at the deep site (**Fig. 3.2** and **Fig. 3.3**). C/N ratios between the upper and

deeper water depths differed by 1.4 in November (**Fig. 3.2**). Additionally, the difference of $\delta^{15}N$ between two sampling depths varied with seasons, and POM sampled 2 m above the sediments was more enriched in ^{15}N in summer but more depleted in ^{15}N during the rest of the year (**Fig. 3.3**).

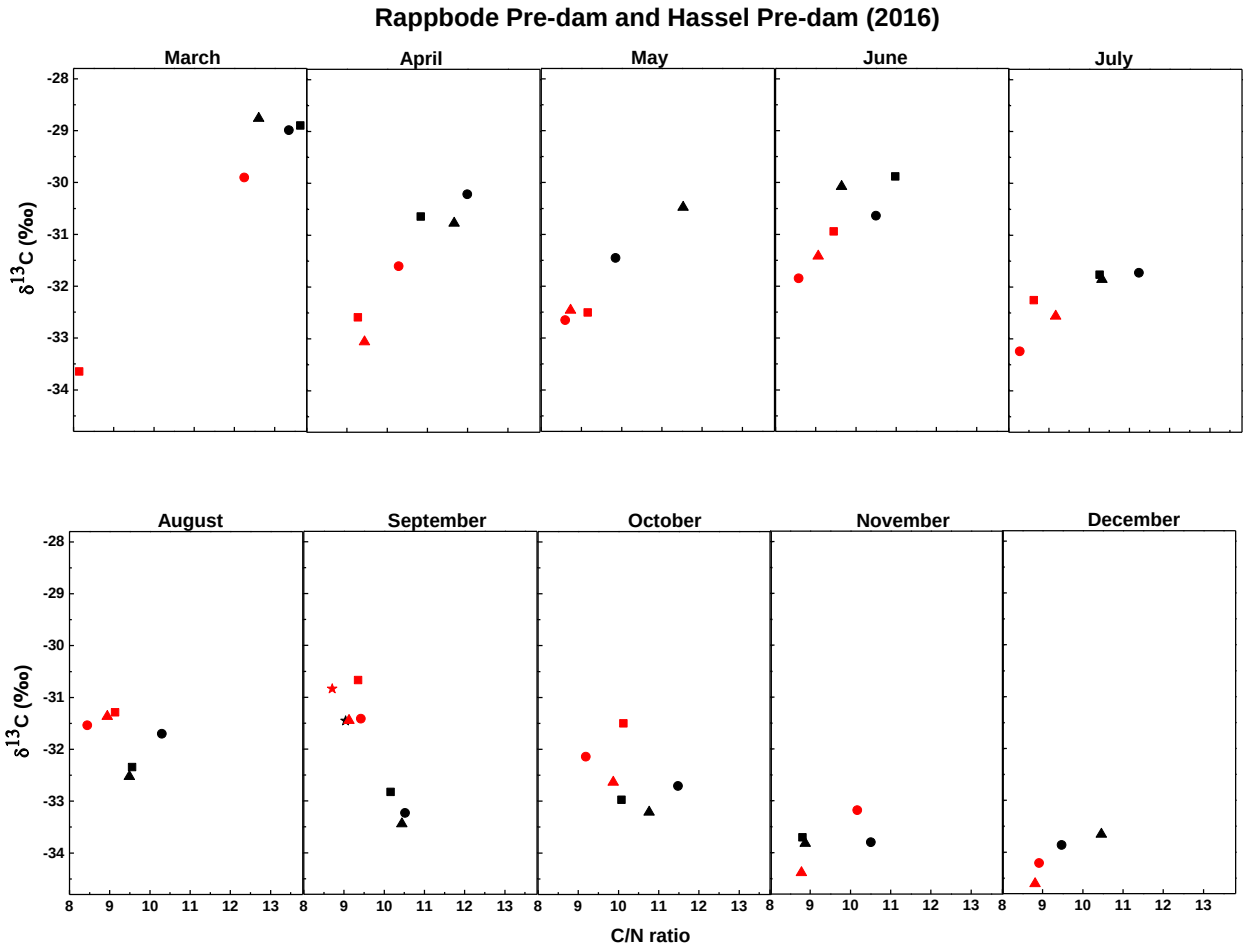


Fig. 3.2 Monthly stable carbon isotopic compositions and atomic C/N ratios of suspended and sediment trap material in Rappbode and Hassel pre-dam. Black and red symbols represent samples taken from Rappbode and Hassel pre-dam, respectively. Squares indicate sediment trap material collected at the shallow sites at a water depth of 3 m; triangles represent sediment trap material collected at the deep sites 6 m under the water surface; circles represent sediment trap material collected at the deep sites 2 m above the ground; stars represent suspended material collected from surface water at the deep sites of both pre-dams.

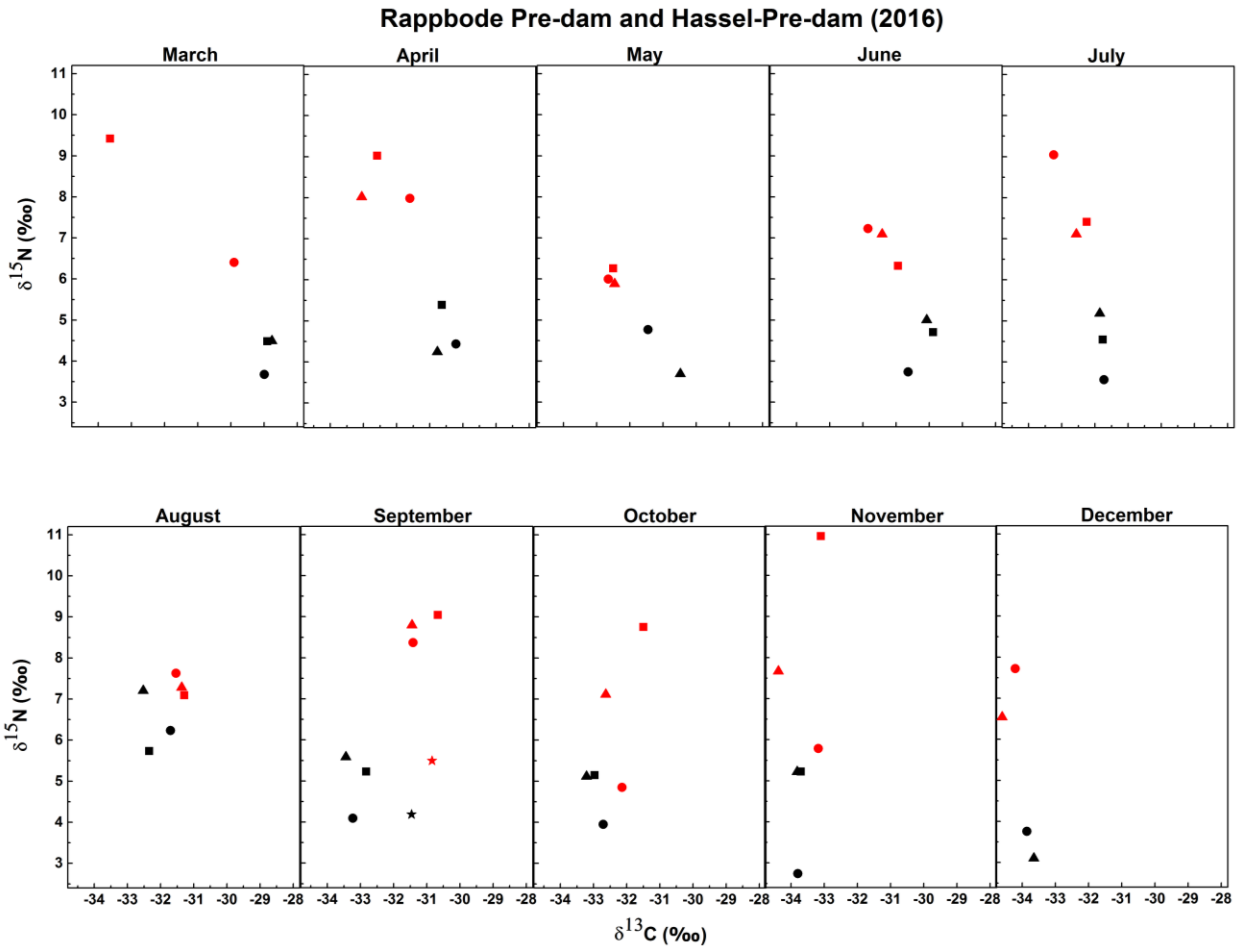


Fig. 3.3 Monthly stable carbon and nitrogen isotopic compositions of suspended and sediment trap material in Rappbode and Hassel pre-dam. Black and red symbols represent samples taken from Rappbode and Hassel pre-dam, respectively. Squares represent sediment trap material collected at the shallow sites at a water depth of 3 m; triangles represent sediment trap material collected at the deep sites 6 m under the water surface; Circles indicate sediment trap material collected at the deep sites 2 m above the ground; stars represent suspended material collected from surface water at the deep site of both pre-dams.

3.2 Biogeochemistry of bulk sedimentary organic matter

3.2.1 Alterations of C and N contents in sediment cores

The distributions of C and N in sediment cores were largely consistent at all sampling sites, including the deep and shallow sites in Rappbode and Hassel pre-dam (**Fig. 3.4**). However, sediments in the upper 10 cm at the shallow site and 14 cm at the deep site in Hassel pre-dam were richer in C and N than the corresponding sediments in Rappbode pre-dam (**Fig. 3.4**). For instance, C and N contents at the deep site of Hassel pre-dam ranged between 107 mg g^{-1} and 88 mg g^{-1} and between 12 mg g^{-1} and 9 mg g^{-1} in the upper 14 cm sediments, whereas they ranged between 87 mg g^{-1} and 77 mg g^{-1} and between 9 mg g^{-1} and 8 mg g^{-1} in the same sediment layer in Rappbode pre-dam. This indicated that intensive degradation of sedimentary OM occurred at the deep sites of both pre-dams, as C and N contents in sediment cores decreased rapidly in the upper 20 cm (**Fig. 3.4**). Degradation of sedimentary OM was also observed at the shallow sites of both pre-dams. Yet, the degradation was found in surface sediments in Rappbode pre-dam while in the middle of the core in Hassel pre-dam.

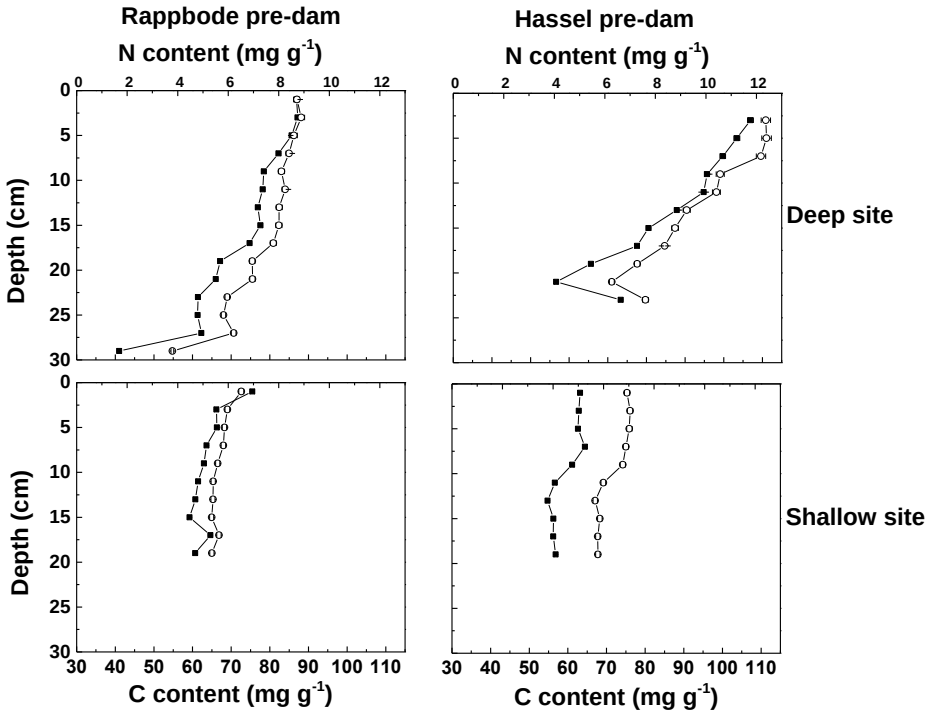


Fig. 3.4 Carbon (solid squares) and nitrogen (open circulars) contents (mg in one gram dry particles) in the sediment cores. Error bars for standard deviations calculated from three replicates (see Chapter 2.5 and **Fig. 2.2**) are not visible in the graph.

3.2.2 Alterations of geochemical proxies in sediment cores

C/N ratios and $\delta^{15}N$ values differed apparently between Hassel and Rappbode pre-dam (**Fig. 3.5**). C/N ratios varied from 9.5 to 11.4 in Hassel pre-dam and from 11.0 to 13.5 in Rappbode pre-dam (**Fig. 3.5a**). Furthermore, a Student's t-test demonstrated significantly higher C/N ratios at the shallow site and also the deep site in Hassel pre-dam ($P<0.001$). Further, the C/N ratios of sediments differed largely between the deep and shallow sites in both pre-dams (**Fig. 3.5a**). Sediments at the deep sites were characterized by a C/N ratio around 11 for Rappbode and 10 for Hassel, whereas the ratio increased at the shallow sites to 13 for Rappbode and to almost 11 for Hassel. The $\delta^{15}N$ values in Hassel pre-dam were on average 1.5‰ higher than those in Rappbode pre-dam (**Fig. 3.5b**). These differences were statistically significant between the two shallow sites ($P<0.001$) and also between the two deep sites ($P<0.001$) as indicated by Student's t-tests. However, $\delta^{13}C$ values were indistinguishable between the two pre-dams and ranged roughly from -31.2‰ to -27.2‰ in both pre-dams.

At the shallow sites of Rappbode and Hassel pre-dam, C/N as well as $\delta^{13}C$ and $\delta^{15}N$ values of OM were fairly constant throughout the sediment cores (**Fig. 3.5**). The $\delta^{13}C$ values ranged from -29.3‰ to -28.7‰ for Rappbode and -29.8‰ to -28.4‰ for Hassel sediments. The $\delta^{15}N$ values varied from 3.7‰ in surface sediments to 4.6‰ at the deepest point of the sediment core in Rappbode pre-dam and from 5.6‰ to 6.8‰ in the sediment core in Hassel pre-dam. Similarly, C/N ratios altered by only 0.6 in Rappbode and 1.0 in Hassel pre-dam. By contrast, the persistent transformation of sedimentary OM took place at the deep sites of both pre-dams, accompanied with the alterations of various biogeochemical proxies. The $\delta^{13}C$ values in the sediment core at the deep sites increased slightly in the upper 0-14 cm in Hassel pre-dam and 0-18 cm in Rappbode pre-dam (**Fig. 3.5a**). Below the depth of 14 cm, sedimentary $\delta^{13}C$ values dropped from -27.2‰ to -29.3‰ in Hassel pre-dam. In Rappbode pre-dam, however, $\delta^{13}C$ values of sediments below 18 cm were virtually constrained to -28.2‰ (**Fig. 3.5a**). An increase of 2.1‰ (from 4.6‰ to 6.6‰) and 2.6‰ (from 2.9‰ to 5.5‰) in term of $\delta^{15}N$ is shown in **Fig. 3.5b** at the deep sites of Hassel and Rappbode pre-dam, respectively. Moreover, C/N ratios increased by 1.5 in Rappbode pre-dam and by 1.7 in Hassel pre-dam (**Fig. 3.5a**).

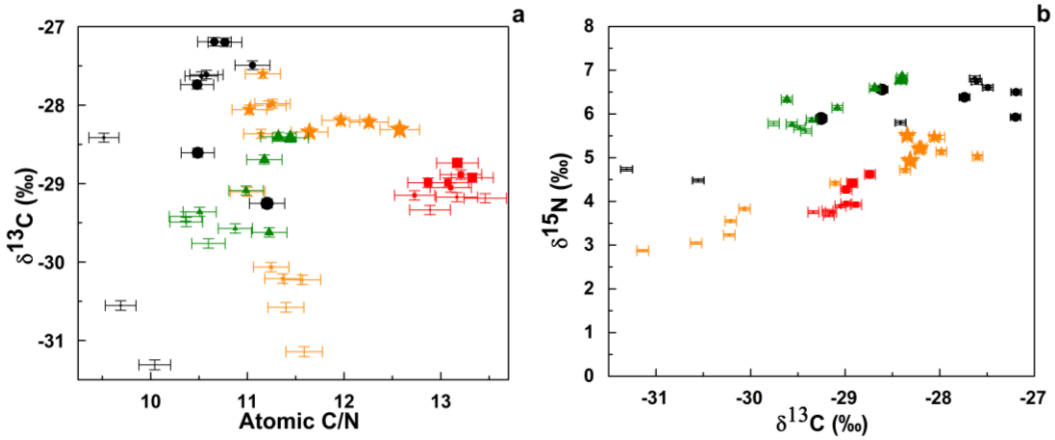


Fig. 3.5 (a) Stable carbon isotopic composition and atomic C/N ratio in sediment cores. (**b)** Stable nitrogen and carbon isotopic compositions in sediment cores. Black circles represent sediments at the deep site of Hassel pre-dam; olive green triangles represent sediments at the shallow site of Hassel pre-dam; orange stars indicate sediments at the deep site of Rappbode pre-dam; red squares represent sediments at the deep site of Rappbode pre-dam. Symbols are enlarged with increasing sediment depth. Error bars for standard deviations were calculated from three replicates. For samples without replicates, standard deviations were calculated from the deviation rate in each sediment core (see Chapter 2.5 and **Fig. 2.2**).

3.3 Biochemical characterization of chemical fractions

3.3.1 Elemental and isotopic compositions of organic matter in chemical residues and extracts

Extraction with hot water dissolved approximately 5% of total OC (TOC in original sediment) and 8% of total N (TN in original sediment) from the untreated bulk sediments (**Fig. 3.6**). Relative to untreated sediments, hot water unextractable residue has a lower $\delta^{13}C$ value by 0.2‰ and higher $\delta^{15}N$ value by 0.5‰ (**Fig. 3.7**). Even though these variations were not statistically significant, hot water extracted OM was still considered as a ^{13}C-enriched and ^{15}N-depleted portion in untreated bulk sediments. It was partly testified by the analysis of carbon stable isotopic composition in hot water extract, for which an enrichment of 0.4‰ in $\delta^{13}C$ value was detected in the extract compared to the resistant residue (**Table 3.1**).

Table 3.1 Elemental concentration and carbon stable isotopic composition in extracts

Organic matter	C (mmol L^{-1})		$\delta^{13}C$ (‰)	
	1 M HCl [a]	6 M HCl [b]	1 M HCl [a]	6 M HCl [b]
Hot water extracted	33.73±3.05		-28.12±0.14	
HCl extracted	69.48±2.72	86.59±5.18	-27.67±0.11	-27.22±0.1
H_2O_2 extracted	15.46±2.09	15.25±5.39	-25.38±0.09	-26.23±0.53
$Na_2S_2O_8$ extracted	1.1±0.03	1.19±0.02	-22.79±0.35	-24.25±0.42

Results were given as means ± standard deviations (n=3).

[a] Group of extracts which was treated with 1 M HCl in the step of acid hydrolysis.

[b] Group of extracts which was treated with 6 M HCl in the step of acid hydrolysis.

To compare the impact of acid concentration on the efficiency of this sequential fractionation procedure, 6 M HCl and 1 M HCl were applied in parallel for the acid hydrolysis of sediments (**Fig. 2.3**), which gave rise to distinctive extraction performances (**Table 3.1**, **Fig. 3.6** and **Fig. 3.7**). OC contents were reduced by 6.7 mg g^{-1} (11% of TOC) and 10.8 mg g^{-1} (18% of TOC) after the hydrolysis with 1 M HCl and 6 M HCl, respectively. About 22% of TN was removed by hydrolysis with 1 M HCl, and the removal efficiency was twofold for 6 M HCl (**Fig. 3.6b**), which leads to the higher C concentration in the 6 M HCl extract (**Table 3.1**). Both $\delta^{13}C$ and $\delta^{15}N$ values depleted significantly (P<0.005) for 6 M HCl resistant sedimentary OM. Therefore, OM extracted by 1 M HCl and 6 M HCl had higher carbon stable isotopic compositions than the untreated bulk sediments (**Table 3.1**). Sediments treated with 1 M HCl caused less evident variations in terms of $\delta^{13}C$ and $\delta^{15}N$, but were still statistically significant (P<0.005). The variations of elemental and stable isotopic compositions (**Fig. 3.6** and **Fig. 3.7**) demonstrated that HCl hydrolyzable OM was mainly N-containing organic compounds. Furthermore, it was relatively ^{13}C-enriched compared to hot water unextractable residue, which was also confirmed by the higher $\delta^{13}C$ in HCl extracts (**Table 3.1**).

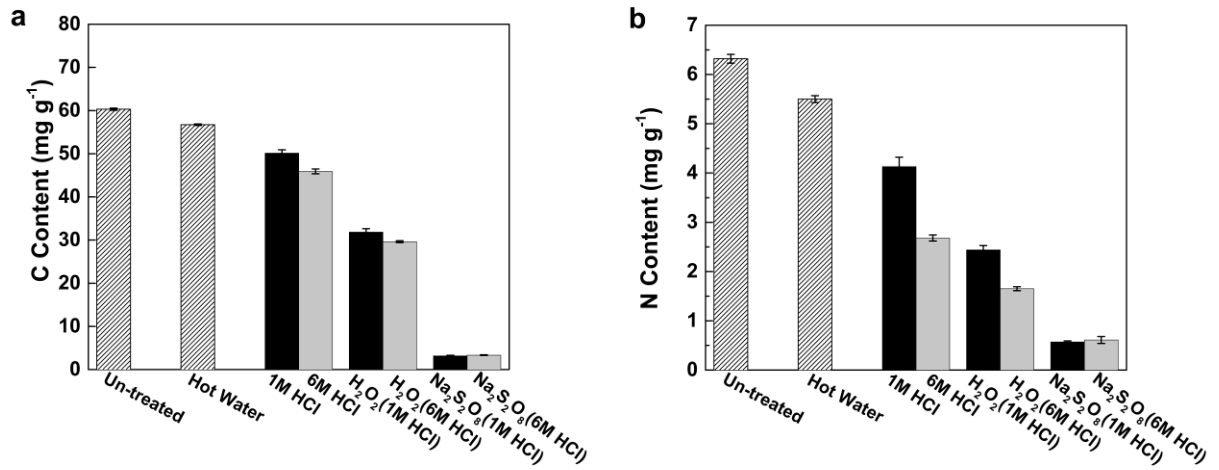


Fig. 3.6 (a) Variations of carbon contents in chemical resistant residues during the sequential fractionation procedure. (**b)** Variations of nitrogen contents in chemical resistant residues with the proceeding of sequential fractionation procedure. Labels with brackets represent this step is after the 1 M HCl or 6 M HCl extraction. Error bars represent standard deviations, of which original bulk sediments and hot water resistant residue had six replicates, while the others had three replicates.

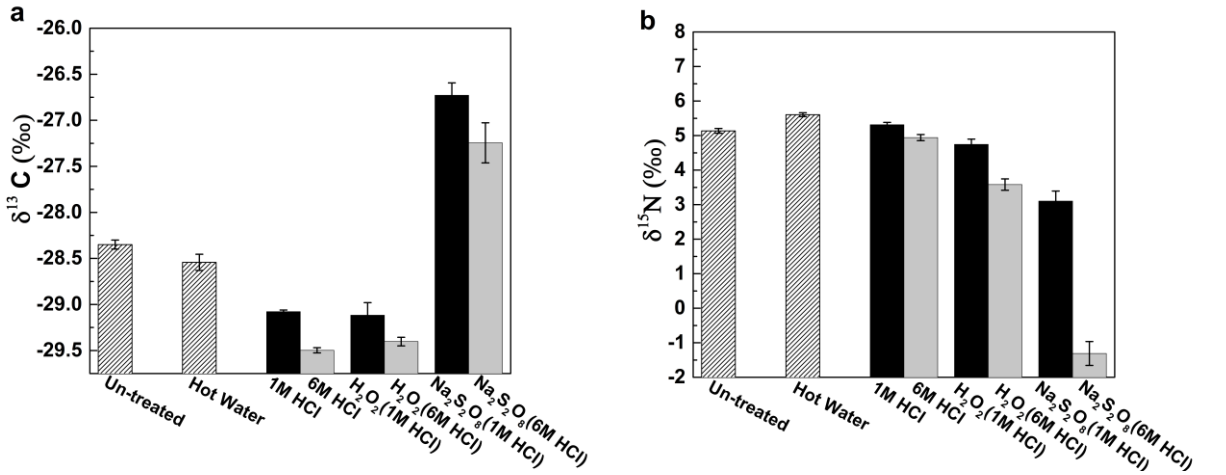


Fig. 3.7 (a) Variations of carbon stable isotopic composition in chemical resistant residues with ongoing sequential fractionation procedure. (**b)** Variations of nitrogen stable isotopic composition of chemical resistant residues with the proceeding of sequential fractionation procedure. Labels with brackets represent this step is after the 1 M HCl or 6 M HCl extraction. Error bars represent standard deviations, of which original bulk sediments and hot water resistant residue had six replicates, while the others had three replicates.

H_2O_2 oxidation led to an intensive reduction of OC and N in the remaining sediments. Regardless of the HCl concentration, H_2O_2 oxidized approximately half of TOC from both 1 M HCl and 6 M HCl treated residues (**Fig. 3.6a**). A majority of the OM was oxidized into CO_2 instead of being dissolved due to the low C concentrations in the extracts (**Table 3.1**). H_2O_2

oxidation caused significantly (P<0.001) greater N loss for 1 M HCl treated residues (about 27%) than for 6 M HCl treated residues (16%). Organic compounds oxidized by H_2O_2 and those retained in residue were indistinguishable in terms of carbon stable isotopic composition, implying that the $\delta^{13}C$ value of H_2O_2 oxidized OM and HCl resistant OM were similar (**Fig. 3.7b**). As the HCl resistant residue had a $\delta^{13}C$ value which was more negative than untreated bulk sediments, the $\delta^{13}C$ value of H_2O_2 oxidized OM was supposed to be more positive than untreated bulk sediments. In contrast to the variation in $\delta^{13}C$, $\delta^{15}N$ decreased from 4.9‰ to 3.6‰ for 6 M HCl treated residue and 5.3‰ to 4.7‰ for 1 M HCl treated residue (**Fig. 3.7b**). The difference of $\delta^{15}N$ shifts significantly differed between 6 M and 1 M HCl treated sediments (P<0.05) based a Student's t-test. Thus H_2O_2 oxidized OM was proposed to be isotopically enriched in ^{15}N than OM in untreated bulk sediments.

As the final step of the fractionation procedure, a majority of the retained OM in H_2O_2 resistant residues was oxidized by $Na_2S_2O_8$ (**Fig. 3.6**). In total, approximately 95% of OC and 90% of N were eliminated by the four-step fractionation procedure. The extraordinarily low C concentration in $Na_2S_2O_8$ extracts (**Table 3.1**) indicated the transformation of OM into CO_2. This caused the high $\delta^{13}C$ value in the extracts and the increases of $\delta^{13}C$ values in $Na_2S_2O_8$ resistant residues. There was no evident difference of C content between the two groups of $Na_2S_2O_8$ resistant residues (1 M HCl and 6 M HCl; **Fig. 3.6**). The shifts in $\delta^{13}C$ were similar between 6 M and 1 M HCl treated $Na_2S_2O_8$ resistant residues, showing a difference of 0.2‰ (**Fig. 3.7a**). Nevertheless, a significant difference (P<0.001) was detected for the shifts in $\delta^{15}N$, as the 6 M HCl treated sediments dropped by 5.2‰, while the1 M HCl treated sediments dropped by 1.7‰ during $Na_2S_2O_8$ oxidation (**Fig. 3.7b**). These substantial variations in stable isotope ratios indicated that the oxidized OM fraction had a lighter carbon stable isotopic composition and a heavier nitrogen isotopic composition than the untreated bulk sediments.

3.3.2 Correlation of C/N ratios and stable isotope ratios in chemical resistance residues

To assess the impact of OM removals on the carbon and nitrogen stable isotopic compositions of the remained OM in bulk sediments, C/N ratios of the chemical resistant residues were plotted against $\delta^{13}C$ values and $\delta^{15}N$ values, respectively (**Fig. 3.8**). C/N ratios decreased steadily by the treatments with hot water, HCl and H_2O. This indicates that

N-containing organic components are more susceptible to chemical degradation (**Fig. 3.8**). The $\delta^{13}C$ was negatively correlated with the C/N ratio, and both correlations for 1 M HCl and 6 M HCl groups were significant (P<0.005) via Pearson correlation tests. However, there was no significant correlation between $\delta^{15}N$ and C/N ratio for chemical resistant residues obtained from this sequential fractionation procedure.

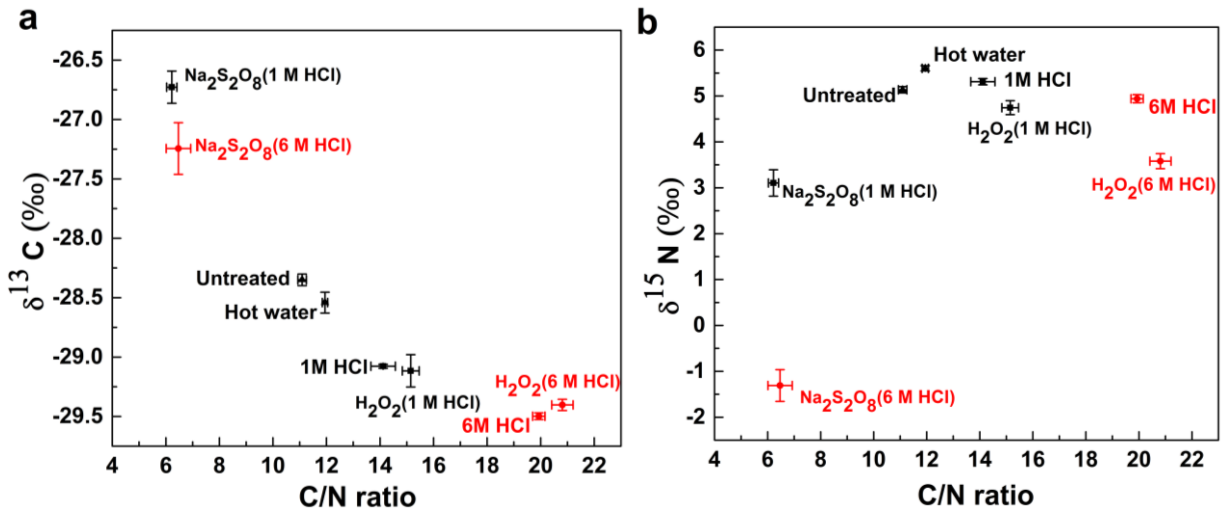


Fig. 3.8 (a) Correlation between carbon stable isotopic composition and atomic C/N ratio in original sediment and residues obtained in sequence from the fractionation procedure (Hot water, HCl, H_2O_2, $Na_2S_2O_8$). **(b)** Correlation between nitrogen stable isotopic composition and atomic C/N ratio in original bulk sediments and residues obtained in sequence from the fractionation procedure. Labels with brackets represent this step is after the 1 M HCl or 6 M HCl extraction.

3.3.3 Chemical structural compositions of chemical resistant residues

Owing to the high chemical complexity of the bulk sediments, the signal-to-noise ratio of ^{13}C NMR spectra was relatively low for untreated and hot water treated sediments (**Fig. 3.9**). Untreated sedimentary OM was dominated by alkyl compounds and contained roughly equal proportion of OC with N-alkyl, O-aromatic and aromatic structures (**Table 3.2**). Carboxyl OC constituted one-eighth of total sedimentary OC (**Fig. 3.9**). By analyzing the signal peaks of chemical shifts with reference to literature, the biomacromolecular organic compounds in untreated sediments were identified. Resonance in the vicinity of 22 ppm can be assigned to long-chain methyl and methylene OC in fatty acids, waxes or resins (Jagadamma et al., 2009; Vane et al., 2005). The peak at 65 ppm corresponded to proteins or carbohydrates which were usually overlapped in this vicinity (Baldock et al., 1992). Resonances arising from O/ O_2-alkyl

carbons that peaked at 87 ppm and 97 ppm were attributed to the most prominent polysaccharides or carbohydrates with anomeric carbons (Baldock et al., 2004; Vane et al., 2005). Resonance occurring at 127 ppm was interpreted as lignins (Hatcher, 1987), and resonance at 166 ppm was assigned to carboxyl, ester and amide compounds (Monteil-Rivera et al., 2000).

Signal peaks in the ^{13}C NMR spectrum of hot water treated residue overall did not shift apparently compared to untreated sediments (**Fig. 3.9**). Nonetheless, signal areas in the regions of 45-60 ppm, 60-95 ppm and 145-165 ppm shrank slightly after the extraction by hot water (**Fig. 3.9**). The integration of ^{13}C NMR spectrum displayed the subtle reduction towards the proportions of N-alkyl, O-alkyl and O-aromatic organic compounds (**Table 3.2**), which decreased by 1.4%, 1.8% and 1.5%, respectively. This hot water dissoluble fraction included aliphatic compounds, amides or amino acids, and water soluble aromatic hydrocarbons. The enrichment of alkyl and aromatic compounds were thus assumed to arise from the removal of the other components.

Hydrolysis with HCl extracted amino acids, polysaccharides and carbonyls from sediments as the signal intensities were markedly reduced in the vicinities of 45-95 ppm and 165-210 ppm (**Fig. 3.9**). The extent of reduction differed between sediment samples treated with 1 M HCl and 6 M HCl (**Fig. 3.9** and **Table 3.2**). A sharp resonance peak at 22 ppm and a broad peak at 121 ppm occurred in the ^{13}C NMR spectrum of the 6 M HCl resistant residue (**Fig. 3.9a**). Therefore, alkyl C made up half of the total OC in 6 M HCl resistant residue, and the proportion of aromatic C increased to one-sixth (**Table 3.2**). Three peaks in the vicinities of 48 ppm, 65 ppm and 79 ppm replaced two broad peaks in the spectrum of hot water unextractable residue (**Fig. 3.9a**). Most probably, these three resonances probably arose from the decomposition products of aliphatic proteins, aliphatic alcohols and complex carbohydrates with ring carbons (Jagadamma et al., 2009; KoÈgel-Knabner, 2002; Norwood et al., 1987). O-alkyl and carboxyl compounds were reduced in 1 M HCl resistant residue, as their abundances declined from 15.3% to 10.5% and 8.0% to 5.3%, respectively (**Table 3.2**). Besides, moderate removal of aromatic compounds was also observed. In general, the losses of organic compounds by 1 M HCl were remarkably smaller than those by 6 M HCl.

As presented in the section of 3.3.1, approximately half of the OC was oxidized by H_2O_2. Therefore, the ^{13}C NMR spectra of the H_2O_2 resistant residues (**Fig. 3.9**) exhibited variations

compared to spectra of residues obtained from fractionation by HCl (**Fig. 2.3**). Peaks at 48 ppm and 79 ppm in the ^{13}C NMR spectrum of the 6 M HCl resistant residue were eliminated. Furthermore, the resonance of aromatic carbon was largely weakened and gave rise to the increased signal intensity at 22 ppm (**Fig. 3.9a**). Although the relative proportion of alkyl C increased, its absolute amount in residue decreased considering the 50% loss of OC caused by H_2O_2 oxidation (**Fig. 3.6**). Changes in OC distribution were also detected in 1M HCl treated H_2O_2 resistant residue. Unlike the occurrence of a sharp peak after the hydrolysis of 6 M HCl, the peak at 22 ppm was prominently strengthened after H_2O_2 oxidation (**Fig. 3.9b**). As a consequence, the relative proportion of alkyl C in bulk sediment increased to over 50% (**Table 3.2**). Except for the large decrease of aromatic C, the proportion of other organic compounds did not change obviously (**Table 3.2**).

Table 3.2 Relative distribution of OC functional groups in sediment fractions through the fractionation procedure. Data are integration results of ^{13}C NMR spectra

Functional group	Un-treated (%)	Hot-water extraction (%)	Acid hydrolysis (%)		H_2O_2 oxidation (%)		$Na_2S_2O_8$ oxidation (%)	
			1M HCl	6M HCl	1M HCl	6M HCl	1M HCl	6M HCl
Alkyl C	40.15	40.92	43.90	50.42	51.86	60.89	28.68	31.60
N-alkyl C	9.22	7.90	8.61	5.84	7.55	4.54	8.70	3.43
O-alkyl C	17.18	15.33	10.51	8.54	8.98	8.40	28.00	27.50
O_2-alkyl C	4.45	4.91	8.27	7.94	5.96	4.50	4.32	6.74
Aromatic C	10.50	13.86	15.07	15.50	10.88	11.76	13.94	15.30
O-aromatic C	10.56	9.08	8.37	7.38	8.66	4.89	12.12	2.41
Carboxyl C	7.94	8.00	5.27	4.37	6.12	5.03	4.24	2.63

Within $Na_2S_2O_8$ resistant residue, there was almost no obvious signal in the ^{13}C NMR spectra as a result of the thorough removal of OM (**Fig. 3.6**and **Fig. 3.9**). Only two weak resonance signals in the chemical shift regions of alkyl C and N-substituted alkyl C were detected in the ^{13}C NMR spectra of both 1 M HCl and 6 M HCl treated $Na_2S_2O_8$ resistant residues (**Fig. 3.9**). They might be long-chain aliphatic macromolecules such as cutans or algaenans (22 ppm), with highly aromatic and aliphatic structures and lignin-like compounds (80 ppm) (Derenne and Largeau, 2001; KoÈgel-Knabner, 2002), which are assigned to be the most recalcitrant components and decomposition products, respectively.

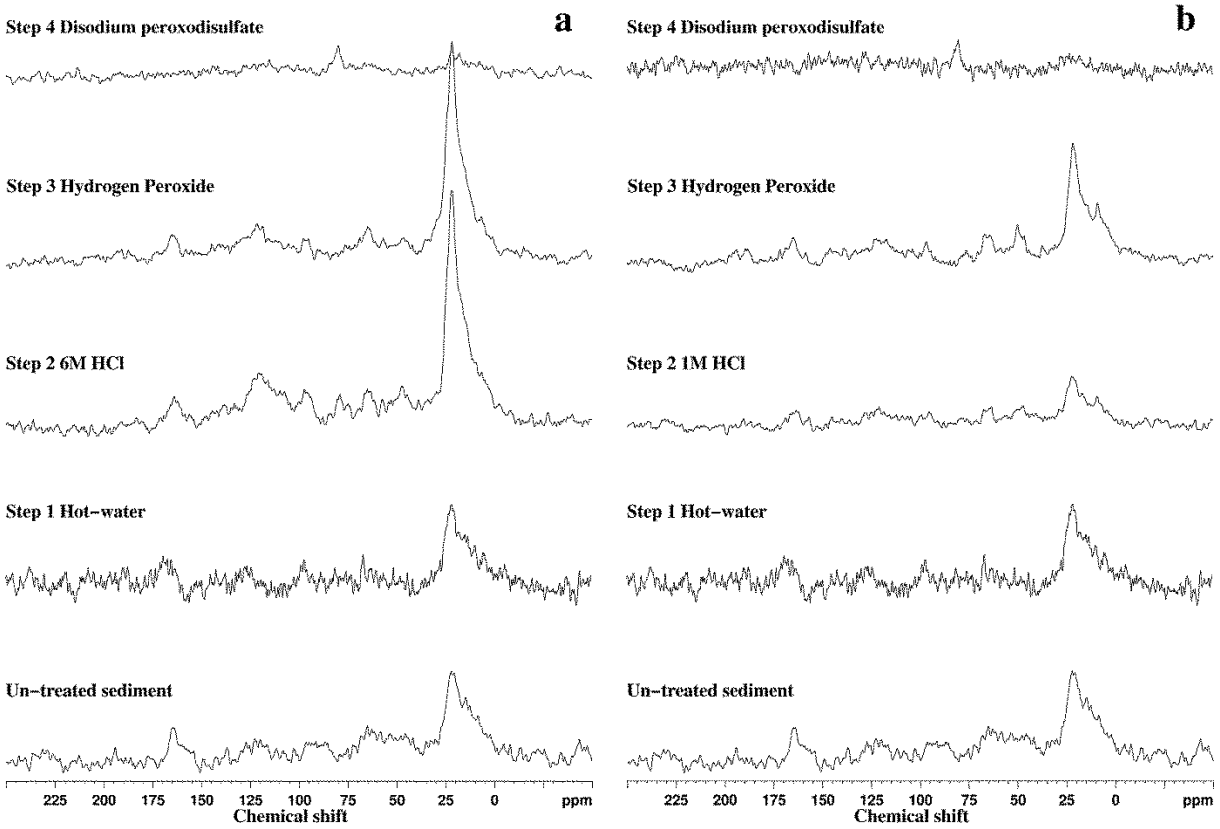


Fig. 3.9 ^{13}C NMR spectra of original bulk sediments chemical resistant residues obtained from sequential fractionation procedure, with which (a) 6 M HCl or (b) 1 M HCl was used for acid hydrolysis.

3.4.4 Changes of biomacromolecular composition of chemical resistant residues

The relative proportions of six major organic components in various residues obtained from the fractionation procedure were calculated from the ^{13}C NMR distributions of OC (**Table 3.2**) by using the mixing model described in Nelson and Baldock (2005). The general biomacromolecular compositions of carbohydrates, proteins, lignins, lipids, carbonyls and chars in residues are given in **Table 3.3**.

Chars and carbonyls were not detected in untreated bulk sediments. Lipids, proteins and lignins dominated the OM in sediments, whereas carbohydrate constituted less than 15% of total OC (**Table 3.3**). The proportions of carbohydrates and proteins slightly decreased with the extraction of hot water, while the proportion of lipids increased by about 2%. Dramatic reduction of carbohydrates and proteins occurred during acid hydrolysis, in particular in sediments treated with 6 M HCl. Part of the lignins and recalcitrant proteins was removed by further oxidation with

H_2O_2. As a consequence, the proportion of lipids increased almost twofold in H_2O_2 resistant residue compared to the untreated bulk sediments. The biomacromolecular composition of 1 M HCl treated H_2O_2 resistant residue was similar to that of 6 M HCl resistant residue (**Table 3.3**). In 1 M HCl and 6 M HCl treated $Na_2S_2O_8$ residues, only analogous of decomposition products, such as proteinaceous and lignin-like remained.

Table 3.3 Relative proportions (in percentage) of carbon assigned to main organic components in sediments. Data are derived from the results of ^{13}C NMR analysis, which is determined from a mixing model developed by Nelson and Baldock (2005)

Organic component	Untreated (%)	Hot water (%)	Acid hydrolysis (%)		H_2O_2 oxidation (%)		$Na_2S_2O_8$ oxidation (%)	
			1M HCl	6M HCl	1M HCl	6M HCl	1M HCl	6M HCl
Carbohydrates	13.29	10.81	2.67	0.00	0.80	0.00	25.67	30.94
Proteins	28.19	26.06	22.13	15.69	20.63	15.03	5.03	48.31
Lignins	23.43	23.11	33.35	26.21	24.13	11.88	39.49	4.94
Lipids	35.09	37.27	41.85	54.84	54.44	68.54	29.82	15.81
Chars	0.00	2.75	0.00	3.27	0.00	4.55	0.00	0.00
N/C ratio	0.09	0.08	0.07	0.05	0.07	0.05	0.16	0.15

3.4 Elemental and stable isotopic compositions of sedimentary organic matter fractions

3.4.1 Depth profiles of chemical isolated OM fractions in sediment cores

Hot water removable OC in sediments constituted 5-15% of total OC (OC in untreated bulk sediments) at the deep site and 3-13% of total OC at the shallow site of Rappbode pre-dam (**Fig. 3.10a**). The corresponding OC contents ranged from 5.1 mg g^{-1} (surface sediments) to 8.7 mg g^{-1} (14-16 cm sediment layer) at the deep site. However, an increase of hot water removable OC with sediment depth (from 2.0 mg g^{-1} to 9.8 mg g^{-1}) was detected at the shallow site (**Fig. 3.10a**). HCl hydrolyzable OC was constrained between 8 mg g^{-1} and 22 mg g^{-1} (**Fig. 3.10a**), and it represented 9-22% of total OC in the untreated bulk sediments. A Student's t-test indicated a significantly higher content of HCl hydrolyzable OC at the deep site compared to the shallow site in Rappbode pre-dam (P<0.01). A negative second-order polynomial relationship (R^2=0.796) was found between HCl hydrolyzable OC content and sediment depth at the deep site. H_2O_2 oxidizable OC varied largely between the deep and shallow sampling sites,

and they made up 54-68% of total OC (**Fig. 3.10a**). Moreover, the down-core reduction of H_2O_2 oxidizable OC at the deep site was 29.3 mg g^{-1}, whereas it was only 5.2 mg g^{-1} at the shallow site. Less than 15% of total OC was removed by $Na_2S_2O_8$ (**Fig. 3.10a**), due to the successive treatments with hot water, HCl and H_2O_2. A steady reduction in $Na_2S_2O_8$ oxidizable OC with sediment depth was detected at the deep and shallow sites.

N content profiles of various OM fractions in Rappbode pre-dam are shown in **Fig. 3.10b**. The proportion of hot water removable N varied between 3% and 18% in the sediment core at the deep site and between 4% and 12% at the shallow site. HCl hydrolyzable N was in general an order of magnitude higher than hot water extractable N, and more than half of total N (50-60%) was extracted by HCl. H_2O_2 oxidizable N made up about one-quarter of total N. Sediments at the deep site had significantly larger proportions of H_2O_2 oxidizable N than those at the shallow site (P<0.005, Student's t-test), similar to the findings for H_2O_2 oxidizable OC. The vertical pattern of H_2O_2 oxidizable N was rather homogeneous at the shallow site with N contents in a narrow range of 1.4-1.7 mg g^{-1}. A broader range of H_2O_2 oxidizable N (0.8-2.4 mg g^{-1}, **Fig. 3.10b**) was observed at the deep site. The portion of H_2O_2 oxidizable N was higher in the upper 0-16 cm sediment layer than in the layers below (**Fig. 3.10b**), confirming the degradation of this N fraction within sediments. The fraction of $Na_2S_2O_8$ oxidizable N was extremely small (between 0.1-0.4 mg g^{-1}), which was smaller than the fraction of hot water extractable N. At the deep site, $Na_2S_2O_8$ oxidizable N was more abundant in the layer of 0-16 cm than in the layers below in Rappbode pre-dam. Consequently, a negative linear relationship (R^2=0.885) was found at the deep site of Rappbode pre-dam by using polynomial regression analysis.

In Hassel pre-dam, hot water, HCl, H_2O_2 and $Na_2S_2O_8$ removed 4-7%, 9-21%, 54-72% and 5-13% of total OC at the deep site, and correspondingly, those proportions were 0.3-10%, 15-21%, 60-68% and 8-12% at the shallow site (**Fig. 3.10a**). The sediment core at the deep site was on average richer in hot water extractable OC by 1.6 mg g^{-1} than the shallow site. Sediments in the upper 0-6 cm of both the deep and shallow sites were characterized by higher HCl hydrolyzable OC content than those below this layer (**Fig. 3.10a**). In particular, the difference increased to 10 mg g^{-1} at the deep site. Nevertheless, a down-core negative second-order polynomial relationship (R^2=0.730) was assigned between HCl hydrolyzable OC and sediment depth at the shallow site. In addition, the amount of H_2O_2 oxidizable OC was significantly higher

(P<0.001, Student's t-test) at the deep site than at the shallow site. Although the contents of H_2O_2 oxidizable OC at the shallow site decreased linearly (R^2= 0.719) with sediment depth, the down-core variation was only 4.1 mg g^{-1} at the shallow site compared to 24.7 mg g^{-1} at the deep site (**Fig. 3.10a**). Linear decreasing trends (R^2=0.744 and 0.849 for the deep and shallow sites) were observed for $Na_2S_2O_8$ oxidizable OC with regard to sediment depth at both the deep and shallow sites.

Sediments in Hassel pre-dam were dominated by HCl hydrolyzable N. The percentage was the same (52-60%) at the deep site and the shallow site. Besides, about a quarter of total N was assigned to H_2O_2 oxidizable fraction, and hot water and $Na_2S_2O_8$ removable N constituted together less than one-quarter of total N in bulk sediments (**Fig. 3.10b**). Hot water removable N varied largely with sediment depth, of which the greater contents were determined in the layer of 6-16 cm (one order of magnitude greater than the other depths, **Fig. 3.10b**). However, sediments in the 0-6 cm layer were richer in HCl removable N versus sediments below this layer, thus the hydrolyzed N contents of surface sediments were two times as high as the sediments at the deepest point in the core. The content of H_2O_2 oxidizable N was significantly greater in the sediment core at the deep site than at the shallow site (P<0.001, Student's t-test). This N fraction was highly steady at the shallow site but decreased from 3.5 mg g^{-1} to 1.7 mg g^{-1} vertically at the deep site (**Fig. 3.10b**). Being revealed by polynomial regression analyses, a second-order decreasing trend with sediment depth (R^2=0.810) was found in $Na_2S_2O_8$ oxidizable N at the deep site but not at the shallow site.

On average an amount of 1.8 mg g^{-1} at the deep site of Rappbode pre-dam and 2.3 mg g^{-1} at the deep site of Hassel pre-dam remained by the end of sequential fractionation procedure (Appendix, Figure 1). This fraction of OC became even smaller at the shallow sites, with mean values around 1 mg g^{-1} in both pre-dams (Appendix, Figure 1). There was almost no N retained in the residues (around 0.5 mg g^{-1}) at all depths in all sediment cores after the consecutive treatments with the four chemicals.

In comparison, H_2O_2 oxidizable OC contents of sediments were significantly higher in Hassel than in Rappbode pre-dam (P<0.005 at the deep site and P<0.001 at the shallow site; Student's t-test). At the deep sites, moreover, the content of HCl hydrolyzable N in surface sediments in Hassel pre-dam was by 2.3 mg g^{-1} higher than in Rappbode pre-dam. A Student's t-

test indicated that this fraction of N was larger at both sites of Hassel pre-dam (deep site $P<0.005$; shallow site $P<0.05$) compared to Rappbode pre-dam.

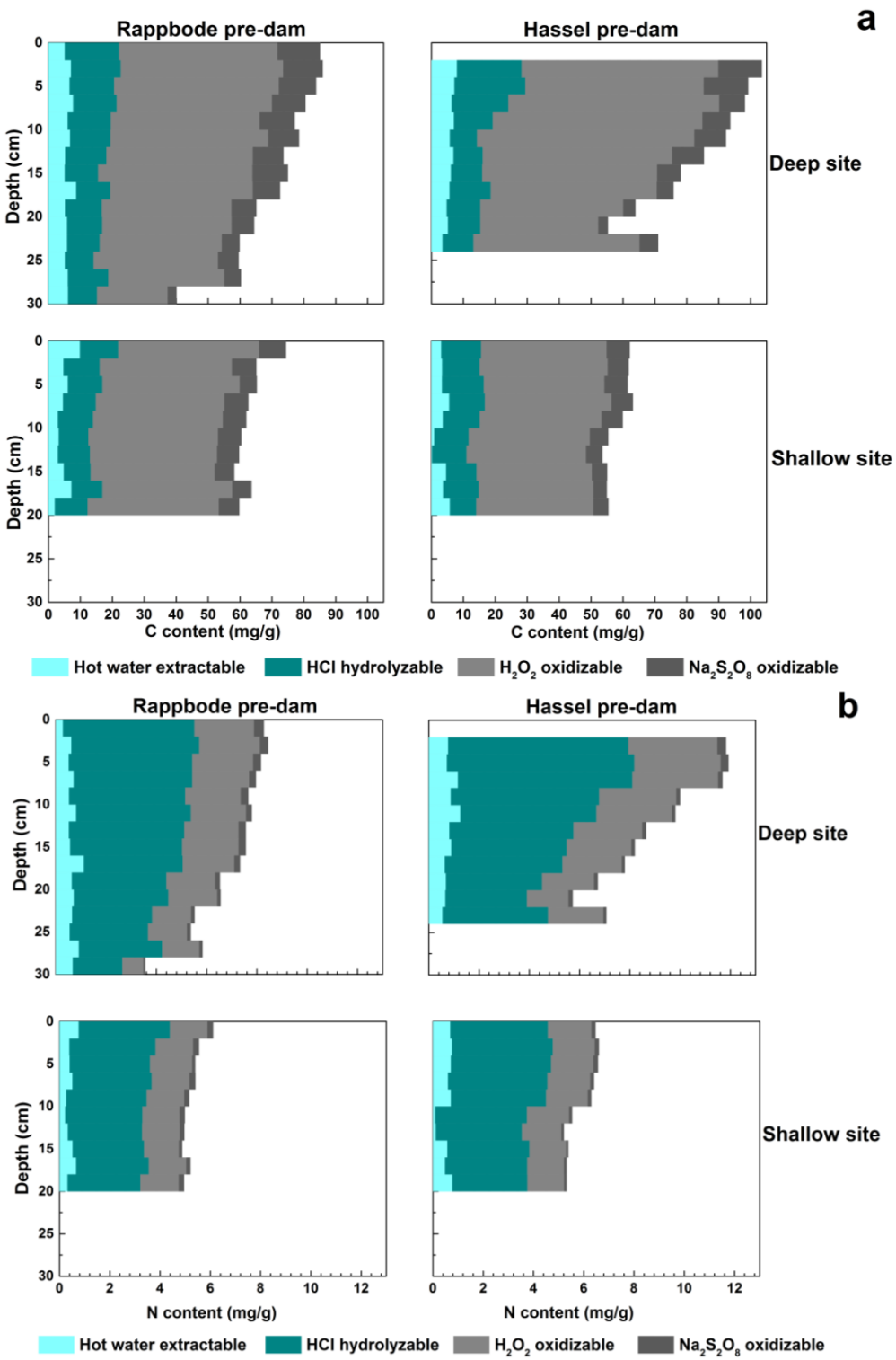


Fig. 3.10 Variations of carbon (**a**) and nitrogen (**b**) contents (mg in one gram of dry sediments) isolated by four fractionation steps (indicated by the color code).

3.4.2 Stable isotope ratio depth profiles of chemical resistant fractions in sediment cores

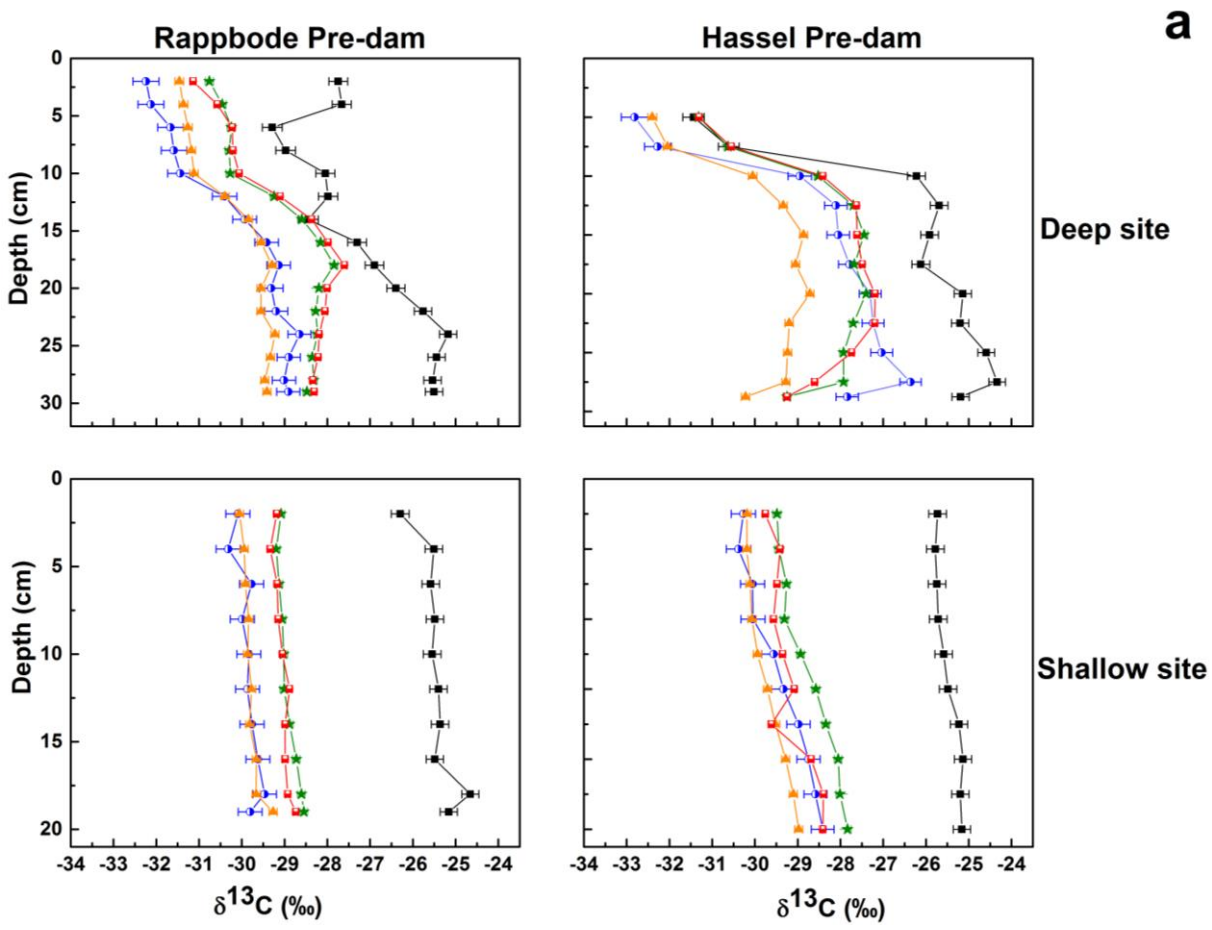
Each fractionation step caused either statistically significant or marginal alterations of stable carbon and nitrogen isotopic composition in the sediments. These alterations were either negative or positive at different sampling sites and sediment depths, depending on the type and magnitude of removed organic components (**Fig. 3.11**).

Hot water extraction did not yield significant alterations in $\delta^{13}C$ at the deep and shallow sites of both pre-dams. These alterations were less than 0.4‰ in Rappbode pre-dam and less than 0.6‰ in Hassel pre-dam (**Fig. 3.11a**). The vertical pattern of $\delta^{13}C$ in hot water resistant residues was in accordance with the pattern in untreated bulk sediments (**Fig. 3.11a**). Furthermore, these alterations were generally positive at the deep sites while negative at the shallow sites (**Fig. 3.11a**), which could be related to the greater OC and N losses at the deep sites (3.4.1). Hot water extraction only caused indistinct alterations of $\delta^{15}N$ in sediment cores in both pre-dams (**Fig. 3.11b**).

HCl hydrolysis of hot water resistant residue led to alterations in $\delta^{13}C$ value for sediments collected from both pre-dams. At the deep sites, greater stable isotopic alterations were observed in the middle 10-22 cm layer in Rappbode pre-dam and in the 4-12 cm layer in Hassel pre-dam. The greatest down-core difference of $\delta^{13}C$ alteration was 0.75‰ for Rappbode and 0.55‰ for Hassel (**Fig. 3.11a**). At the shallow sites, the alterations were generally less than 1‰ throughout the sediment core in Rappbode pre-dam but greater than 1‰ from the depth of 10 cm in the sediment core in Hassel pre-dam (**Fig. 3.11a**). HCl hydrolysis caused alterations of $\delta^{15}N$ value as high as 2.7‰ (at the deepest depth of the sediment core) at the shallow site of Hassel pre-dam and 1.7‰ at the shallow site of Rappbode pre-dam (**Fig. 3.11b**). Alterations in $\delta^{15}N$ of HCl resistant residues overall exhibited an increasing down-core trend at the deep and shallow sites in both pre-dams (**Fig. 3.11b**). Considering the decreasing trend of HCl removable N with the increasing sediment depth (**Fig. 3.10b**), the extent of $\delta^{15}N$ change was proposed to be negatively related to removed N content.

Contrary to the large reduction of OC caused by H_2O_2 oxidation (**Fig. 3.10a**), there was no significant alteration in $\delta^{13}C$ (**Fig. 3.11a**). The vertical pattern of $\delta^{13}C$ alteration differed largely between the deep and shallow sites and between the two pre-dams. At the deep site of Rappbode

pre-dam, $\delta^{13}C$ increased in sediments of 0-14 cm layer but decreased in 14-29 cm layer (**Fig. 3.11a**). In Hassel pre-dam, positive alteration occurred only in the upper 6 cm sediments, and the alteration turned to be negative below the depth of 6 cm and enlarged with sediment depth (**Fig. 3.11a**). At the shallow sites in both pre-dams, less obvious variations (one order of magnitude less than at deep sites) were observed (**Fig. 3.11a**). The alterations were only noticeable below the depth of 8 cm at the shallow site of Hassel pre-dam. However, **Fig. 3.10b** shows a significant difference between both pre-dams with regard to the $\delta^{15}N$ alterations (P<0.005 at deep sites and also shallow sites) resulting from the oxidation by H_2O_2. In Hassel pre-dam, $\delta^{15}N$ at the deep site changed only slightly in the upper 6 cm layer and altered by 1.3‰ to 3.0‰ below this layer. It increased by 1.4‰ from the surface sediments and by 2.0‰ at the deepest point of sediment core at the shallow site, which was comparable with the alterations in sediment cores at the deep site. In Rappbode pre-dam, $\delta^{15}N$ decreased at the deep and shallow sites, but the decreases were overall less than in Hassel pre-dam.



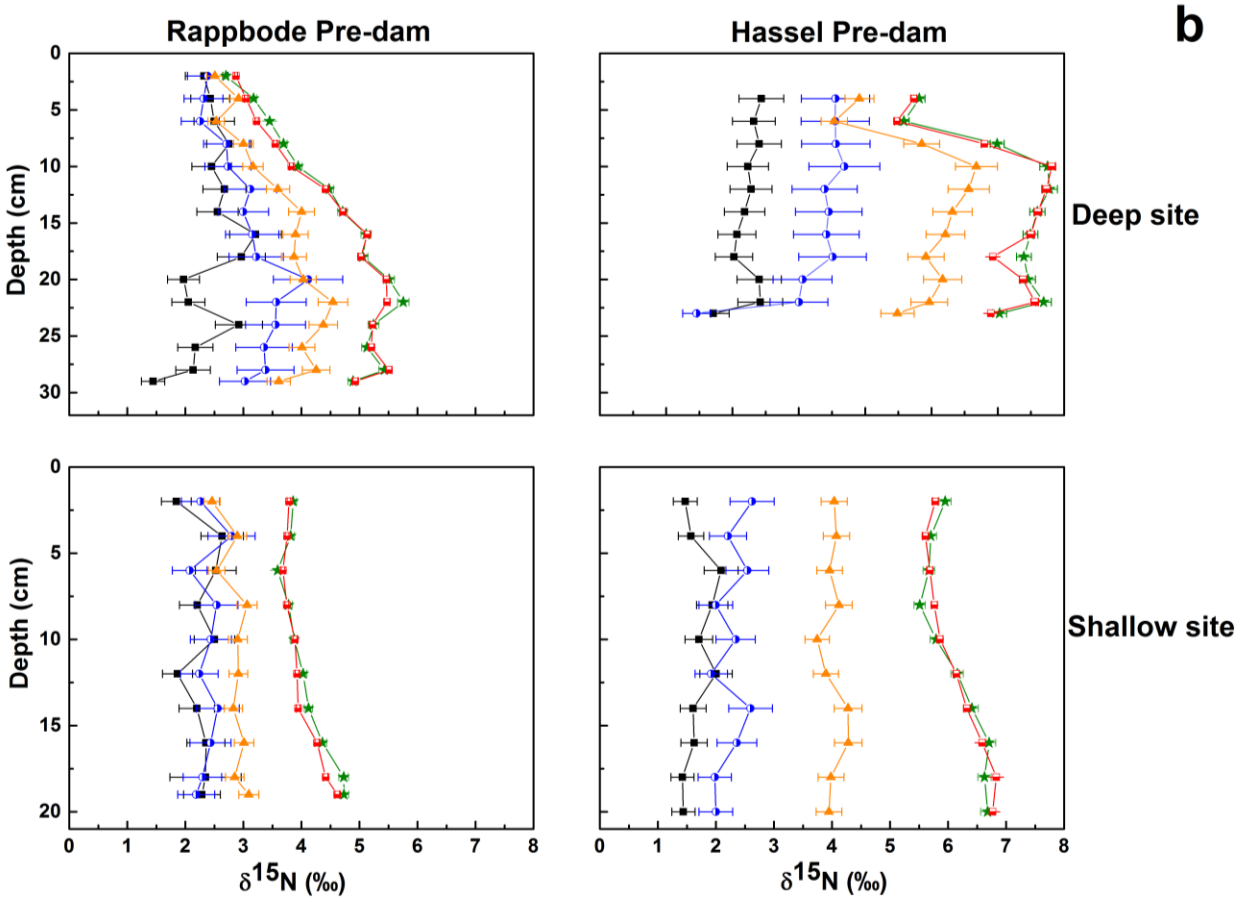


Fig. 3.11 Alterations of stable carbon (**a**) and nitrogen (**b**) isotopic composition in original bulk sediments and chemical resistant residues with the proceeding of fractionation procedure and sediment depth. Sediments were sampled from cores at the deep and shallow sites of Rappbode and Hassel pre-dams. Red lines with squares represent original bulk sediments; green lines with stars represent hot water resistant residue; orange triangles indicate HCl resistant residue; purple circles represent H_2O_2 resistant residue; black squares indicate $Na_2S_2O_8$ resistant residue. Error bars represent standard deviations (n=3). For samples without replicates, standard deviations were calculated from the deviation rate in each sediment core (Chapter 2.5 and **Fig. 2.2**).

Alterations of $\delta^{13}C$ value caused by $Na_2S_2O_8$ oxidation were relatively constant in the sediment cores at the shallow sites, which varied positively by 3.8-4.8‰ in Rappbode pre-dam and by 3.3-4.6‰ in Hassel pre-dam (**Fig. 3.11a**). In addition, a linearly decreasing trend regarding the $\delta^{13}C$ variation (R^2=0.971) in the sediment core was observed via polynomial regression analysis at the shallow site of Hassel pre-dam. At the deep site of Rappbode pre-dam, however, the positive alteration varied from 1.5‰ in sediments at the depth of 12-14 cm to 4.5‰ in surface sediments. The $\delta^{13}C$ values of $Na_2S_2O_8$ resistant residues were higher by 1.4-2.7‰ than those at the deep site of Hassel pre-dam. Regarding the alteration of $\delta^{15}N$, it was only

conspicuous in the 0-18 cm layer at the deep site of Hassel pre-dam as well as in 18-29 cm layer at the deep site of Rappbode pre-dam (in general ≥1‰). Consequently, the $\delta^{15}N$ of $Na_2S_2O_8$ resistant residue throughout this sediment core was relatively homogeneous.

3.4.3 Characterization of the biomacromolecular composition of organic matter in sediment cores

To facilitate the interpretation of the vertical profiles of stable isotopic compositions in sediment cores, the OC distribution of sedimentary OM was analyzed by solid-state ^{13}C NMR spectroscopy. Based on the results in Section 3.3.3, the OC distributions and stable isotopic compositions of sedimentary OM were roughly unchanged after the extraction by hot water. Furthermore, there was approximately 5% of OC left after the oxidation by $Na_2S_2O_8$, which resulted in a rather weak signal in ^{13}C NMR spectra (**Fig. 3.9**). Hence the biomacromolecular composition of untreated, hot water and $Na_2S_2O_8$ treated sediments were not measured. HCl and H_2O_2 resistant residues at the depth of 14-16 cm were selected for ^{13}C NMR analysis as indicative samples for the understanding of the vertical stable isotopic composition profile in sediment cores.

Resonances of organic compounds in HCl resistant residues from both pre-dams generally peaked at the same vicinities within the ^{13}C NMR spectra (**Fig. 3.12**), indicating that sedimentary OM in these two pre-dams had similar distributions of OC. The peak at 33 ppm (**Fig. 3.12**) was identified as long chain lipids such as waxes, resins and fatty acids (Jagadamma et al., 2009). Peaks at 60 ppm and 76 ppm (**Fig. 3.12**) were attributed to methoxy groups or aliphatic proteins and polysaccharides with ring carbons or alcohols in residues (Hatcher, 1987), respectively, which were usually of terrestrial origin (KoÈgel-Knabner, 2002). Due to the resonating overlaps of these compounds, it was difficult to clarify the specific compounds from the available spectra. Peaks at 133 ppm and 151 ppm (**Fig. 3.12**) in aromatic C region represented the lignins in sediments (Hatcher, 1987). The signals resonating from 169 ppm to 187 ppm and at 198 ppm indicated amides, esters and carbonyls in sediments (**Fig. 3.12**).

The application of mixing model based on the integration results of ^{13}C NMR spectra (Appendix, Table 1) gave rise to the biomacromolecular compositions of HCl and H_2O_2 resistant residues (**Table 3.4**). Overall, all the chemical resistant residues were prominently dominated by

lipids. In particular, C assigned to lipids comprised a larger proportion of total OC in HCl resistant residues at the deep sites relative to the shallow sites of both pre-dams. OM at the shallow sites of both pre-dams was generally richer in lignins than OM at the deep sites, of which the proportion of lignins was around one time more abundant at the shallow site of Rappbode pre-dam than the other sampling sites (**Table 3.4**). Proteinaceous C was almost equally distributed in all the HCl resistant residues, and chars were also detected with a percentage varying from 3-10%. In H_2O_2 resistant residues, only lipids and complex proteins were detected with an abundance ratio of 4 to 1 (**Table 3.4**).

Table 3.4 Relative OC distribution of major biomacromolecular components (in percentage, %) in HCl non-hydrolyzable and H_2O_2 inoxidizable fractions in sediment core study

Organic component	Deep-Hassel		Shallow-Hassel		Deep-Rappbode		Shallow-Rappbode	
	HCl	H_2O_2	HCl	H_2O_2	HCl	H_2O_2	HCl	H_2O_2
Carbohydrate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Protein	13.72	19.75	12.84	24.62	12.94	14.53	11.59	22.56
Lignin	20.06	0.00	24.29	0.00	27.23	0.00	45.65	0.00
Lipid	60.02	80.25	53.04	75.38	56.53	85.47	38.56	77.44
Char	6.20	0.00	9.83	0.00	3.29	0.00	2.90	0.00

Data were derived from the results of ^{13}C NMR analysis, which were determined from a mixing model developed by Nelson and Baldock (2005).

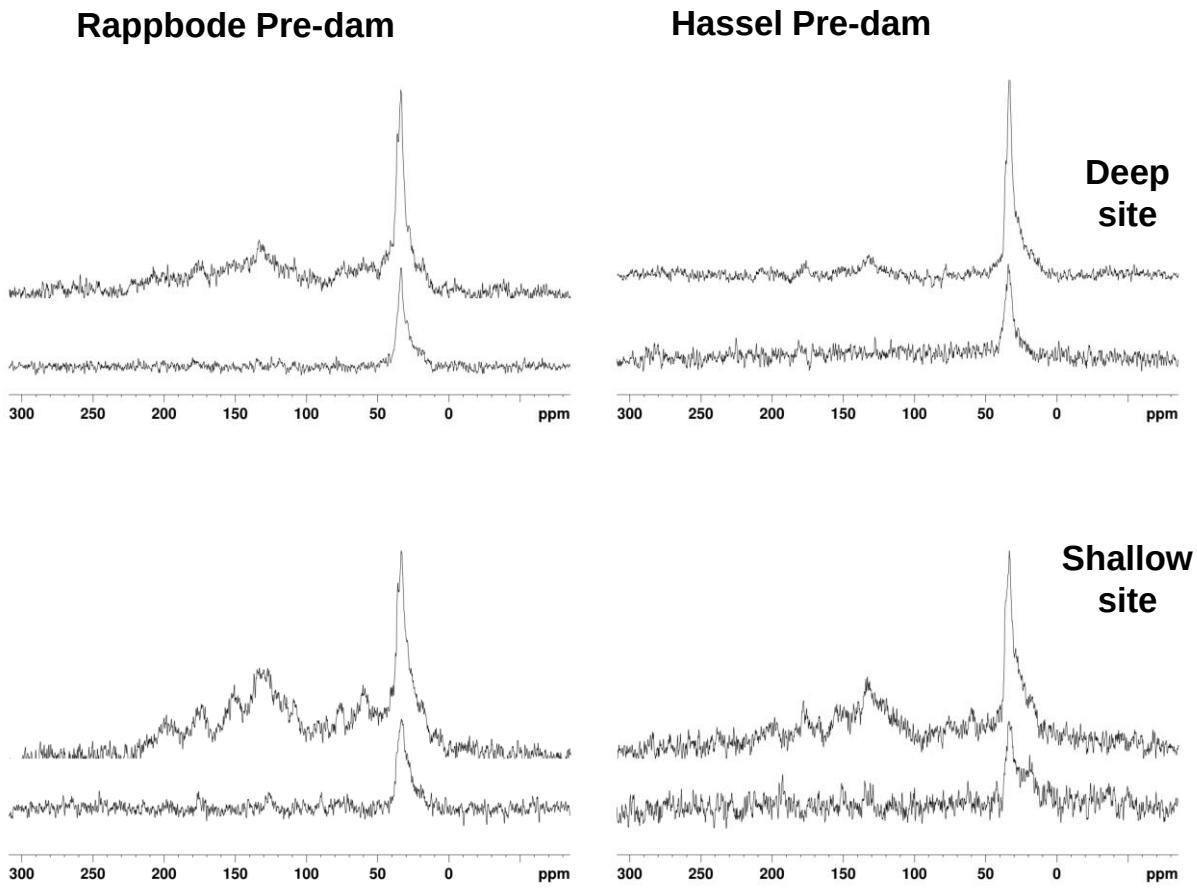


Fig. 3.12 ^{13}C NMR spectra of HCl resistant residues (above) and H_2O_2 resistant residues (below) in Rappbode and Hassel pre-dams. Sediments used for ^{13}C NMR analysis were collected from the depth of 14-16 cm at the deep and shallow sites in both pre-dams.

Chapter 4 Discussion

Sediments are a permanent sink for C and nutrients which is determined principally by two aspects, the net OM inputs (from aquatic and terrestrial origins) and the losses that are caused by microbial degradation. In respect to the aspect, OM sources were identified mainly based on the assays of geochemical proxies in sinking POM and sedimentary OM. Concerning the latter aspect, the degradation of OM in sediments still requires fundamental understanding, such as the underlying mechanisms and their controls. The first part of the discussion evaluates the efficiency of the OM fractionation method. The second part discusses the track the POM dynamics in the water column. The last two parts of the discussion focus on the identification of organic biomacromolecular components in sediments and the estimation of their individual degradation characteristics using the analytical results of chemical fractions obtained from the fractionation procedure.

4.1 Evaluation of the sequential fractionation procedure

As the separation of OM in this work was accomplished by a sequential fractionation procedure, the efficiency of this fractionation method was first assessed by the differences of elemental and isotopic composition among isolated OM fractions. In order to facilitate the application of these proxies for interpreting the OM degradation in sediments, the influence of biomacromolecular composition changes on the biogeochemical proxies (C/N ratio, $\delta^{13}C$ and $\delta^{15}N$) was deciphered.

4.1.1 Selection of HCl concentration for the hydrolysis of sediments

Hydrolysis of the sediments with 6 M HCl resulted in a better fractionation effect than with 1 M HCl owing to the higher simplicity of ^{13}C NMR spectra of 6 M HCl resistant residues (**Fig. 3.9**). The biomacromolecular composition of OM in 1 M HCl resistant residue still showed a high complexity which resulted from the incomplete extraction of proteins and carbohydrates (**Table 3.3**). It further led to a less intense oxidation of lignins by H_2O_2. Therefore, the sequential fractionation procedure using 1 M HCl in the acid hydrolysis step was incapable to identify the organic biomacromolecular components in sediments (**Fig. 3.9**). When 6 M HCl was rather used in the acid hydrolysis step, the complexity of the biomacromolecular composition of sedimentary

OM decreased remarkably by effective removal of proteins, carbohydrates, and lignins (**Fig. 3.9**). A similar comparison had been conducted on soils by Silveira et al. (2008) who demonstrated that 1 M HCl hydrolyzed only a portion of proteins and carbohydrates without evidently simplifying the structure of soil organic matter.

4.1.2 Biomolecular composition of chemical resistant residues

In order to assess the effectiveness of the sequential fractionation procedure that was adopted in this work, OM fractions isolated by each fractionation step were characterized by ^{13}C NMR and elemental analyses. Considering the complexity of the bulk samples and the overlaps in the resonance spectra, the peaks presented in spectra were assigned with the help of literature. The signals in the region of 40-100 ppm are able to be recognized as there are typical chemical shifts representing carbons in carbohydrates, proteins and lignins (Akhter et al., 2016; KoÈgel-Knabner, 2002).

OM in the untreated bulk sediments in Hassel pre-dam was dominated by lipids, lignins and proteins but was depleted in carbonyl and char (**Table 3.3**). This observation is fairly similar to the biomacromolecular composition of OC in freshwater (Lake Washington) sediments which is predicted through a 'Terrestrial' model by Nelson and Baldock (2005). For instance, the predicted proportion of C in lignins is a quarter of total sedimentary OC in Lake Washington, and it is comparable to the corresponding 23% in Hassel pre-dam.

Amino acids and polysaccharides extracted by hot water are assumed to be derived from microbes, referring to the investigations on soils (Ghani et al., 2003; Leinweber et al., 1995). Hot water extraction on Hassel pre-dam sediments resulted in a similar effect that a small fraction of microbial amino acids and polysaccharides was extracted. During the second step of this sequential fractionation procedure, proteins and alcohols, carbohydrates with ring carbons were extracted by HCl. It was in accordance with the increase of C/N ratio from 12 to 20 during HCl hydrolysis (**Fig. 3.8**). HCl hydrolysis exerts similar influences on the composition of soil OM (Rovira and Vallejo, 2002; Silveira et al., 2008), implying that OC fractionation method of soils is also applicable to sediments. Furthermore, despite the nearly unchanged C/N ratio after H_2O_2 oxidation (**Fig. 3.8**), most of the lignins and part of lipids with carboxylic structure (referred to the chemical shift of 165 ppm in **Fig. 3.9a**) were oxidized by H_2O_2. A majority of aliphatic

compounds (resonating at 22 ppm) which probably existed in waxes, steroids and fatty acids were oxidized by $Na_2S_2O_8$. Moreover, a small amount of H_2O_2 resistant OM, lignins with guaiacyl units (122 ppm, 145 ppm), aliphatic protein or xylan and anomeric carbohydrates, was simultaneously removed during $Na_2S_2O_8$ oxidation. These findings confirmed the statement of Jagadamma et al. (2009) that $Na_2S_2O_8$ is more efficient in oxidizing aliphatic compounds from soils compared to H_2O_2.

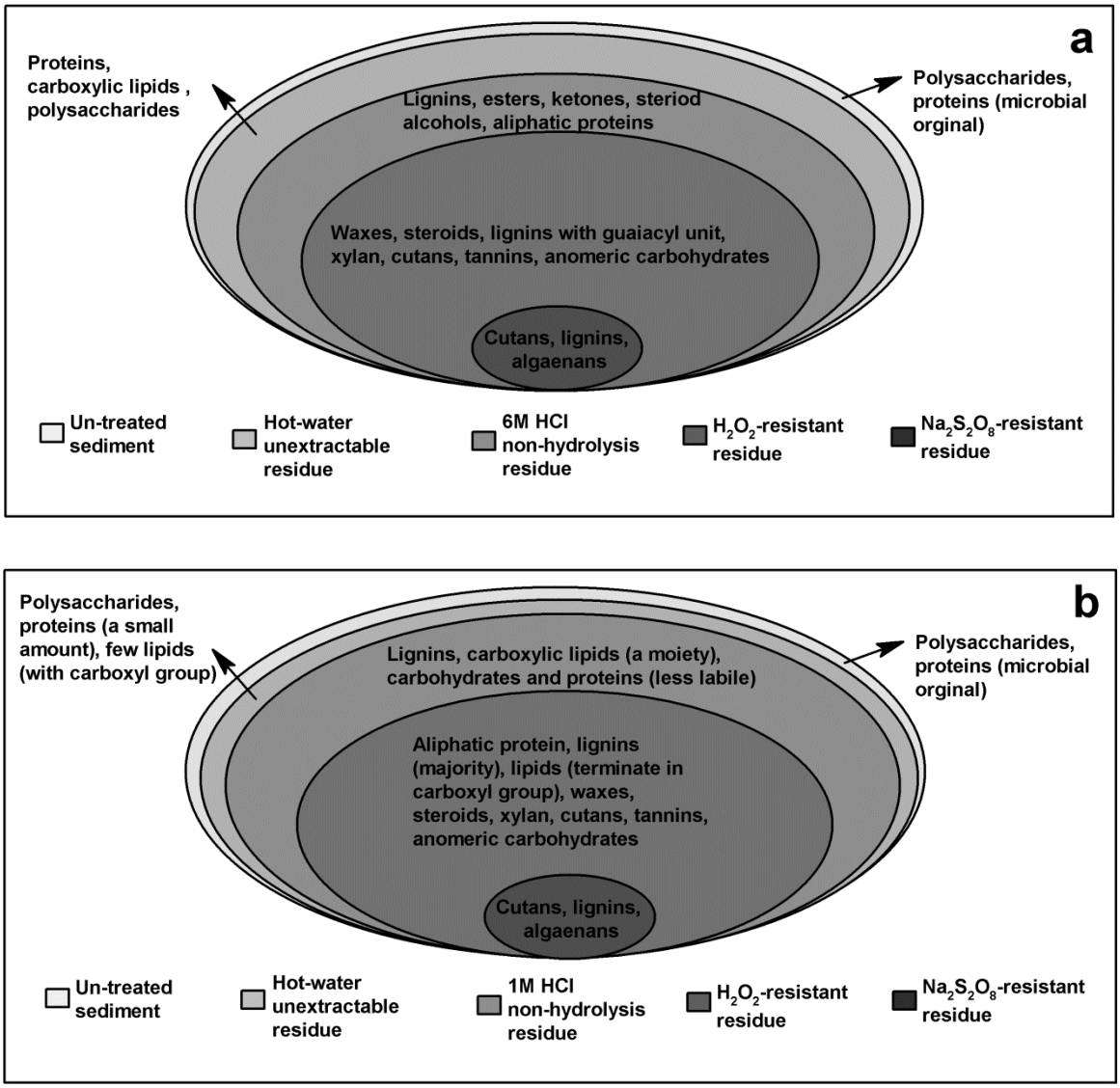


Fig. 4.1 Biomolecular components remained in residues of the OC fractionation group 6 M HCl (**a**) in the acid hydrolysis step and group 1 M HCl (**b**) in the acid hydrolysis step, referring to the chemical shifts in ^{13}C NMR spectra and the predicted results from a mixing model (Table 3.3). The areas of ellipses are in proportion to the magnitude of OM in residues, while the annuluses between two adjacent ellipses represent the OM fractions removed by chemicals.

Due to the inefficient extraction by 1 M HCl in the fractionation procedure, the distribution of OC in HCl and H_2O_2 resistant residues had evidently higher complexity compared to the corresponding residues in 6 M HCl fractionation procedure (**Fig. 3.9b**). It was indicated partly by the higher OC concentration (17.1 mmol L^{-1}) in 6 M HCl extract than in 1 M HCl extract. Hydrolysis with 6 M HCl isolated a fraction of lipids that could neither be extracted by 1 M HCl nor oxidized by H_2O_2 in the next step. This fraction of lipids was able to be completely oxidized by $Na_2S_2O_8$, and therefore, no noticeable difference in OC content was observed between 1 M HCl and 6 M HCl treated $Na_2S_2O_8$ resistant residues. **Fig. 4.1** gives a generalized summary of the biomolecular compositions of the OM in untreated bulk sediments and chemical resistant residues.

4.1.3 Implication for the study of organic matter degradation in sediments

The active fraction of microbial proteins and polysaccharides, the comparatively stable fraction of retained proteins and polysaccharides, as well as the refractory fraction of lignins and lipids were isolated sequentially from sediments by this multistep fractionation procedure. This sequence is consistent with the biochemical recalcitrance (not equal to biological availability) of the major organic components in aquatic and terrestrial environments which confirmed by experimental (McColl and Gressel, 1995) and modeling (Baldock et al., 2004) studies. Hence, the new developed sequential fractionation procedure simulated the natural degradation processes, thereby contributing to the explanation of OM degradation in nature.

Assuming that C/N ratio was an effective indicator for the proportions of aquatic and terrestrial sources in sedimentary OM, its alteration with the multistep fractionation procedure can reveal the variations of the importance of terrestrial and aquatic sources. The C/N ratio of sediment residue kept increasing during the sequential extractions with hot water, HCl and H_2O_2, indicating that algal-derived OM was gradually removed from bulk sediments. However, the rises of C/N ratio caused by hot water extraction and by H_2O_2 oxidation were not as evident as that occurred after the HCl hydrolysis and $Na_2S_2O_8$ oxidation. Different explanations can be given for the slight increase of C/N ratio that caused by hot water extraction and caused by H_2O_2 oxidation. The former was restricted by the limited amount of hot water soluble N-containing OM in sediments. The latter resulted from an evident oxidation of C-enriched compounds such

as lignins and lipids by H_2O_2. Regarding the remarkable increase of C/N ratio after HCl hydrolysis, it was attributed to the relative scarcity of C-enriched carbohydrates and abundance of N-enriched proteins in bulk sediments. Overall, the decreasing trend of organic components revealed by C/N ratio was in good line with the trend deduced from solid-state ^{13}C NMR analysis.

C/N ratio was negatively related to $\delta^{13}C$ values during this fractionation procedure (**Fig. 3.8**), namely $\delta^{13}C$ values declined with the removals of organic compounds from bulk sediments. Knowing the material used for the test of this fractionation method was surface sediments, the relationship between C/N ratio and $\delta^{13}C$ values is proposed to track the temporal rather than spatial changes of sedimentary OM. The shifts of $\delta^{13}C$ value in sedimentary OM are more often used to indicate the alteration of vegetation in the catchment. For example, the switch of dominant agricultural plants from wheat (C3 plants) to sugarcane (C4 plants) in the catchment would cause the enrichment of ^{13}C in sediments (Martinelli et al., 1999). Nevertheless, most of the catchments do not undergo such an intensive vegetation change, so a dramatic shift of $\delta^{13}C$ value (e.g. greater than 10‰) was not common. Consequently, the $\delta^{13}C$ values in sediments were more frequently used for indicating the enrichment of aquatic OM input.

To date, few studies have taken advantage of carbon stable isotopic composition for the study of OM degradation in sediments. In this work, it was found that proteins and carbohydrates were ^{13}C-enriched components compared to the bulk sediments, whereas components such as lignins and lipids with higher chemical recalcitrance were comparatively ^{13}C-depleted. These predictions on the relative carbon stable isotopic compositions of the main organic components are in general consistent with the results obtained by compound-specific stable carbon isotope analyses (A Hobbie and Werner, 2004; Filley et al., 2001; Meyers and Ishiwatari, 1993b; Rieley et al., 1991). Therefore, the degradation of these organic components in sediments can be reflected by the variation of $\delta^{13}C$ value.

During the sequential fractionation of sedimentary OM, the $\delta^{15}N$ value of bulk sediments did not vary linearly like C/N ratio and $\delta^{13}C$ value. It increased slightly after the extraction by hot water and then decreased gradually after the treatments with HCl, H_2O_2 and $Na_2S_2O_8$ (**Fig. 3.7b**). Hot water soluble labile proteins and carbohydrates were assumed to be ^{15}N-depleted relative to bulk sediments, owing to their microbial origin whose $\delta^{15}N$ value ranging from 5‰ to 8‰ (Das et al., 2013). Furthermore, the relatively more ^{15}N-depleted OM in microbes was a consequence

of the microbial consumption of algae that could cause negative stable isotopic fractionation (Lehmann et al., 2002; Macko and Estep, 1984). Other organic components including more stable proteins, carbohydrates, lignins and lipids were relatively ^{15}N-enriched, while most recalcitrant components, such as lignins, cutans and algaenans, were ^{15}N-depleted.

The quantification of an individual organic component variation and the concurrent alteration of stable isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$ values) are of great significance for the interpretation of OM degradation process in sediment cores.

4.2 Accumulation and degradation of sinking particulate organic matter

4.2.1 Aquatic and terrestrial OM inputs to sinking particulate organic matter

To facilitate the comparison among fractions of sinking POM from the shallow and deep sites of different water depths, values of $\delta^{13}C$, $\delta^{15}N$ and C/N ratio in **Fig. 3.2** are plotted against the sampling month (**Fig. 4.2**). C/N ratio and $\delta^{13}C$ values exhibit in general similar trends over the sampling month in both pre-dams, implying that $\delta^{13}C$ value can be employed like C/N ratio for the identification of OM sources. This finding is supported by the case study in the Gulf of Mexico where $\delta^{13}C$ value and C/N ratio evidence consistently a small terrestrial input of OM to the surface sediments (Goñi et al., 1998). There is no obvious difference in the C/N ratios of suspended POM in Hassel and Rappbode pre-dams, and thereby a greater C/N ratio of sinking POM indicates a larger contribution of land plants as sinking POM is a mixture of algal and terrestrial POM. Thus, the sinking POM in Rappbode pre-dam contained a larger proportion of terrestrial sources than that in Hassel pre-dam almost throughout the year (except September and October).

Aquatic plants and land plants assimilate different forms of nitrogen and thus are labeled with distinct nitrogen stable isotope ratios (Meyers and Ishiwatari, 1993b). Aquatic plants are generally characterized by greater $\delta^{15}N$ values than terrestrial plants (Last and Smol, 2006; Schmidt and Gleixner, 2005). Suspended POM in Hassel pre-dam had higher $\delta^{15}N$ (1.3‰) relative to that in Rappbode pre-dam. However, this distinction is readily offset by the difference of $\delta^{15}N$ values of sinking POM between these two pre-dams, since the annual average $\delta^{15}N$ value of sinking POM was 2.4-3.2‰ (from deep to shallow site) higher in Hassel pre-dam than in

Rappbode pre-dam. Several possibilities can be ascribed to the greater $\delta^{15}N$ values of sinking POM in Hassel pre-dam, which are the additional heterotrophs from agricultural discharge (isotopically heavy), the dominance ^{15}N-enriched phytoplankton and the enhanced algal productivity. Given the almost twofold higher C and N contents in suspended POM and the greater C and N contents in sinking POM in Hassel pre-dam (**Fig. 3.1**), it confirms that the comparatively higher productivity is at least one of the attribution for the greater $\delta^{15}N$ values of sinking POM. In consequence, a larger proportion of aquatic sources can be expected in the sinking POM in Hassel pre-dam, which is in accordance with the findings indicated by proxies of $\delta^{13}C$, and C/N ratio (**Fig. 3.2**).

There is an obvious seasonal change in the contribution of aquatic and terrestrial sources to sinking POM in Hassel pre-dam. The $\delta^{13}C$ value of sinking POM elevates in late spring and in late summer at both deep and shallow sites (**Fig. 4.2**). A similar trend was reported previously in Franklin Bay where the $\delta^{13}C$ value of sediment trap material peaked in spring and in summer over the year (Belt et al., 2008). Aquatic OM makes up a greater proportion of sinking POM at the deep site than at the shallow site in warm seasons (May to September). C/N ratio and $\delta^{15}N$ of sinking POM give in general consistent indications in the composition of aquatic and terrestrial sources at the deep site as evidenced by the reverse trends between C/N ratio and $\delta^{15}N$ over the year (**Fig. 4.2**). Reverse trends between C/N ratio and $\delta^{15}N$ of sinking POM are in line with the finding of Teranes and Bernasconi (2000), who have also deployed sediment trap in a small eutrophic lake. The variation of $\delta^{13}C$ value over the year exhibits similar trends in the contribution of aquatic OM, although the indications are less evident than those derived from C/N ratio and $\delta^{15}N$ value.

Concerning the months (e.g. from April to May) that C/N ratio and $\delta^{15}N$ provide contradictory information for OM sources, it is perhaps caused by the extreme weather which has washed more land plants detritus into pre-dam and thereby has decreased the $\delta^{15}N$ value of sinking POM. Fox et al. (2010) have also demonstrated the significant impacts of extreme events on the identification of OM sources through altering the $\delta^{15}N$ value.

4.2.2 Biogeochemistry of particulate organic matter in the water column

The dynamics of POM in the water column is revealed by the comparisons of sediment trap material that has been collected at two water depths at the deep site. **Fig. 4.2** indicates that terrestrial sources contribute a larger portion of POM at the deeper water depth than at the upper water depth in Rappbode pre-dam. Given the lower C and N contents at the deeper water depth, it reflects the rapid degradation of aquatic POM in the water column or the dramatic decrease of primary productivity due to the increased water depth. By contrast, a larger proportion of aquatic POM is observed at the deeper water depth compared to the upper water depth in Hassel pre-dam. In particular, this observation is more evident from June to August when greater C and N contents are detected in sediment trap material (**Fig. 3.1**). This finding is in good accordance with the algae bloom which is usually known to take place in summer in this pre-dam (Friese et al., 2014). It might be evidenced by the great sedimentation rate at the deeper water layer, during the seasons with high primary productivity (Appendix, Table 2).

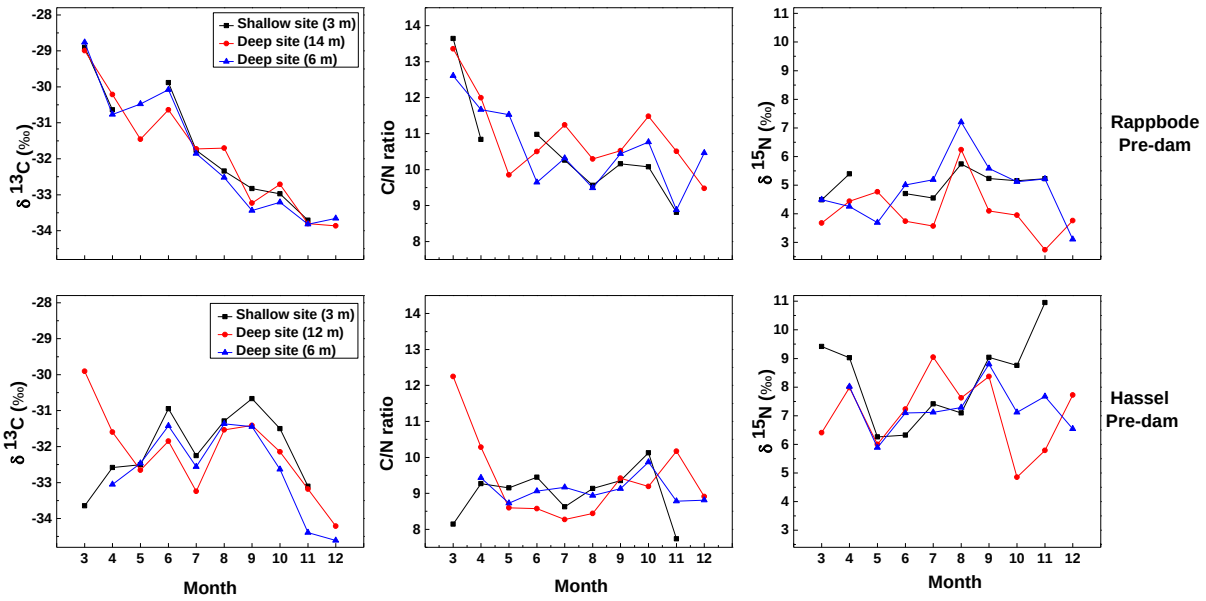


Fig. 4.2 Biogeochemical proxies of sinking POM in Rappbode and Hassel pre-dams in 2016. Black lines with square symbols represent sinking particles sampled at the shallow sites with water depth of 3 m; Blue lines with triangle symbols represent sinking particles sampled at the deep sites which were 6m under the water surface; Red lines with circular symbols represent sinking particles sampled at the deep sites which were 2 m above the bottom of water basin.

Both primary production and OM degradation are supposed to alter the $\delta^{15}N$ value of sinking POM. The sensitivity of $\delta^{15}N$ to the transformation of sinking POM has been demonstrated by Gaye-Haake et al. (2005). Moreover, the causal relationship between the decrease of $\delta^{15}N$ value and the increase of productivity with water depth have been discovered in other studies (Gaye et al., 2009; Lehmann et al., 2002). Most sediment trap studies state that the degradation of planktonic algae will cause the enrichment of ^{15}N in the remained OM (Altabet, 1988; Altabet et al., 1991; Ostrom et al., 1998; Schäfer and Ittekkot, 1993). Therefore, the depletion of ^{15}N in sinking POM at the deeper water depth in Rappbode pre-dam is largely related to the decreased primary productivity rather than the degradation of aquatic POM. $\delta^{13}C$ values of sinking POM can be used for tracing the biogeochemistry of POM in the water column, yet it is comparatively less sensitive than $\delta^{15}N$ to the changes in aquatic productivity.

4.3 Identification of organic matter sources in sediments

4.3.1 Stable isotopic compositions as source indicators of sedimentary organic matter

Sedimentary OM in Hassel pre-dam contains overall a larger proportion of aquatic sources than that in Rappbode pre-dam. The $\delta^{13}C$ and $\delta^{15}N$ values of sediments in the upper 6 cm in Hassel pre-dam are close to the values of algae in the water column, suggesting that OM in this sediment layer is dominated by aquatic sources. OM in surface sediments in Rappbode pre-dam has also a similar $\delta^{13}C$ value with algae, while the $\delta^{15}N$ value is depleted by 1.3‰ compared to algae. It is probably due to the more negative $\delta^{15}N$ value of the terrestrial OM than that of the algae in the water column. The difference of $\delta^{15}N$ value between terrestrial and aquatic sources could be up to 7‰ (Das et al., 2013; Meyers and Ishiwatari, 1993b). Alternatively, the depleted $\delta^{15}N$ value of sediments in Rappbode pre-dam might result from the negative isotopic fractionation being caused by the degradation of algae, or microbial incorporation of ^{15}N-depleted OM sources into sediments (Altabet, 1988; Saino and Hattori, 1980, 1987).

Stable isotopic compositions of sediments at the deep sites are not evidently different from those at the shallow sites in both pre-dams. It is noteworthy that the $\delta^{13}C$ and $\delta^{15}N$ values of the sediments at the shallow sites in both pre-dams overlap with those values of sediments below the depth of 6 cm at the deep sites (**Fig. 3.5b**). Since the sediments below 6 cm at the deep sites are

more depleted in aquatic OM than sediments above this layer, sediments at the shallow sites of both pre-dams are considered to be relatively depleted in aquatic OM.

The selective degradation of a certain organic component, usually the fresh, labile and aquatic fraction, is a critical control on the contributions of aquatic and terrestrial OM sources in sediment cores. Hence, biogeochemical proxies will reflect the variation of composition in terms of OM sources. Knowing the $\delta^{13}C$ and $\delta^{15}N$ values of sedimentary OM at the shallow sites remain relatively constant along the sediment cores (**Fig. 3.5**), it assumes that no apparent degradation of OM has taken place in both pre-dams. At the deep sites, the $\delta^{13}C$ and $\delta^{15}N$ values of sediments increase gradually throughout the core, indicating that the degraded portions of OM are relatively ^{13}C-depleted and ^{15}N-depleted. In consequence, the contribution of aquatic sources in sedimentary OM at the deep sites of both pre-dams declines with the increasing sediment depth.

4.3.2 C/N ratio as source indicator of sedimentary organic matter

In addition to stable isotope ratios, C/N ratio is another effective proxy for the identification of OM sources. To quantify the proportions of aquatic and terrestrial OM in sediments, a two-source mixing equation was adopted (Guillemette et al., 2017; Thornton and McManus, 1994).

$$C/N_{sediment} = fC/N_{terrestrial} + (1-f)C/N_{aquatic} \quad (9)$$

where f is the relative proportion of terrestrial OM in sediments; $C/N_{sediment}$, $C/N_{terrestrial}$, and $C/N_{aquatic}$ correspond to the atomic C/N ratio of the bulk sediments, of the soils from the catchment and of algae. Schönfeldt (2013) determined the soil C/N ratios in the catchments of Hassel and Rappbode pre-dams, which the average value was 13.1 in Hassel and 15.4 in Rappbode pre-dam. C/N ratio of algae was 8.7 and 9.0 in Hassel and Rappbode pre-dam, respectively. These values were applied to Equation (9), and the relative contribution of the terrestrial source in sedimentary OM was then calculated by substituting the C/N ratios in **Fig. 3.2**.

The calculated proportions of terrestrial OM sources at the deep and shallow sites of Hassel and Rappbode pre-dam are given in **Table 4.1**. It is generally in agreement with the prediction

based on stable isotopic compositions (see this section), which the contributions of terrestrial and aquatic sources to sedimentary OM vary largely between two pre-dams, between deep and shallow sites and throughout the whole core.

Hassel pre-dam has accumulated a substantially large proportion of aquatic OM into sediments compared to Rappbode pre-dam. At the shallow site, sedimentary OM is dominated by aquatic sources in Hassel pre-dam while by terrestrial sources in Rappbode pre-dam. At the deep sites of both pre-dams, sediments exhibit the predominance of aquatic OM sources throughout the cores (except the sediments at the deepest 2 cm layer in the core). However, the proportions of terrestrial OM in the upper 8 cm sediments in Rappbode pre-dam are evidently larger than those in the sediments at the same layer in Hassel pre-dam. It could be interpreted as a directly greater terrestrial OM input to Rappbode pre-dam from the catchment or/and a larger contribution of algae or microbes in Hassel pre-dam. The former explanation is evidenced by the greater lignin (exclusively assigned to land plants) contents in the sediments of Rappbode pre-dam as evidenced by the ^{13}C NMR analysis (**Table 3.4**). The latter explanation is supported by the higher primary productivity in the water column and greater microbial biomass which are known in the sediments of Hassel pre-dam (Friese et al., 2014; Wendt-Potthoff et al., 2014).

Terrestrial sources play a more important role in sedimentary OM at the shallow sites than at the deep sites in both pre-dams. Considering the shallow site located near the inflow stream, the accumulation and preservation of terrestrial OM are assumed to be more effective at the shallow sites than that at the deep sites. A higher percentage of lignin in the sedimentary OM at the shallow sites of both pre-dams (**Fig. 3.12**) indicates a larger proportion of terrestrial OM. Moreover, the over three times higher sedimentation rate (Dadi, 2016) and the one order of magnitude less biomass in the sediments at the shallow sites (Wendt-Potthoff et al., 2014), which have been detected in these two pre-dams, explain indirectly the larger proportion of terrestrial sources in sediments. A high proportion of terrestrial OM in sediments is frequently observed at the site near the inflow in inland waters. For example, sedimentary OM at the inflow site of an oligotrophic lake (Constance, Germany) consists almost only terrestrial sources (Wessels, 1998).

The comparatively high proportion of terrestrial OM in the upper 2 cm sediment layer at all of the sampling sites can be ascribed to the inputs of relatively fresh terrestrial detritus of high susceptibility to degradation. This fraction of OM is in general rapidly degraded, so the

proportion of terrestrial OM first decreases slightly. Probably due to the greater degradability of aquatic OM than the remaining terrestrial OM, the proportion of terrestrial OM increases to 55-65% in sediments at the deepest depth of these cores (**Table 4.1**). This pattern of terrestrial and aquatic OM distribution in sediment cores is observed in other modern sediments (younger than 100 years) which have also been revealed by a down-core rise of C/N ratio (Kaushal and Binford, 1999; Meyers and Lallier-Vergès, 1999; Sampei and Matsumoto, 2001). Based on previous findings, the down-core increase of terrestrial OM proportion could be interpreted principally from two perspectives, (1) the selective degradation of aquatic organic components because of their relatively high bioavailability (Guillemette et al., 2017; Khan et al., 2015; Meyers and Ishiwatari, 1993b), and (2) the lower degradation rate in the deep sediments (usually below 15 cm), due to a lack of microorganisms, scarcity of OM and the anoxic environment in the deep sediment layer (Kristensen, 2000; Lehmann et al., 2002; Schwarz et al., 2007).

Table 4.1 Relative contribution of the terrestrial source in sediment cores. Values were calculated from two-source (terrestrial and aquatic) mixing model

Sediment depth (cm)	**Rappbode**		**Hassel**	
	Deep[a]	Shallow	Deep	Shallow
0-2	40.4	69.7	NM	43.0
2-4	37.5	60.8	30.5	37.6
4-6	40.2	65.1	22.5	37.8
6-8	36.9	58.3	18.5	49.3
8-10	35.1	64.1	41.5	40.9
10-12	31.3	65.7	42.7	51.8
12-14	33.5	63.7	53.5	57.3
14-16	35.3	60.5	44.5	56.2
16-18	33.8	67.6	47.0	59.4
18-20	34.7	65.2	40.5	62.2
20-22	31.6	NA	40.6	NA
22-24	46.4	NA	56.9	NA

NM= Sediment at this depth was not measured, because it was consumed by other projects.
NA=Not available due to the limited depth of sediment cores.
[a] Data below the 24 cm sediment layer was not shown.

4.4 Degradation of organic matter in sediments

This section intends to interpret the degradation of sedimentary OM by determining the alterations of biomacromolecular composition in the sediment core. These alterations are mainly caused by the release of OC back to atmosphere via microbial respiration. To obtain the vertical profile of the biomacromolecular composition in sediment cores, sedimentary OM has to be separated into a range of organic components. The elemental and isotopic characteristics of these components will enable the inspection of OM degradation processes.

4.4.1 Degradation of organic components in sediments-evidence from elemental analysis

A multistep fractionation method is proposed to avoid leaving a portion of OM undefined (e.g. black carbon) and allows the identification and quantification of the OM in sediments (Baldock et al., 2004; Burdige, 2007). Instead of extracting a range of known organic compounds (e.g. biomarkers) or classes of biomolecules (e.g., humic substances), sedimentary OM in this work was divided into five fractions via a four steps chemical fractionation method. OM fractions being isolated from different steps of the fractionation procedure contain generally more than one organic biomacromolecular component. The main components in these fractions are still able to be identified by comparing the elemental, stable isotopic and biomacromolecular compositions between two pre-dams and two sampling sites within pre-dams. The abundance and the degradability differ greatly among various organic components (proteins, carbohydrates, lignins and lipids), and thus they are interpreted individually in this section.

Carbohydrates in sediments have comparable bioavailability as proteins (Danovaro et al., 1993; Meyers and Ishiwatari, 1993b). They are assumed to be reduced with the decrease of biota in sediments, since labile carbohydrates and proteins are essential constituents of algae and bacteria. In this work, terrestrial carbohydrates are relatively inactive, because the sums of proteinaceous and saccharous C and N remain almost unchanged in sediment cores at the shallow sites of high molecular weight and chemical structure, such as carbohydrates with anomeric or ring carbons.

It is difficult to quantify the aquatic and terrestrial sources of carbohydrates based on the available results. The ^{13}C NMR analysis of the sediments from the deepest depth or a specific carbohydrates extraction protocol might be helpful to clarify the degradation degree of

carbohydrates. However, given that proteins are N-enriched compounds while carbohydrates contain little N, the vertical profiles of both components can be roughly identified by the changes of C/N ratio of HCl hydrolyzed OM in sediment cores. The minimum C/N ratio of HCl hydrolyzed OM is found around the middle layer of all sediment cores, suggesting that carbohydrates are even more recalcitrant than proteins below the middle sediment layer (12-16 cm at the deep sites and 8-12 cm at the shallow sites). The work of Dell'Anno et al. (2000) supports to some extent this observation by comparing the degradation of proteins and carbohydrates in the surface marine sediments with the sediments at the depth of 15 cm, demonstrating the relatively higher recalcitrance of carbohydrates, especially in the deeper sediments.

Proteins in sediments were predominantly isolated together with carbohydrates by HCl hydrolysis, whereas microbial and some complex proteins were removed from bulk sediments by hot water and H_2O_2, respectively. A predominance of proteins over carbohydrates in sinking POM and sedimentary OM has been observed in many aquatic ecosystems (Kaal et al., 2015; Nelson and Baldock, 2005; Niggemann, 2005). In the reference material (surface sediments in Hassel pre-dam), the results of ^{13}C NMR analysis indicated that the abundance of OC in proteins was one time higher than in carbohydrates (**Table 3.3**). It is noted that C/N ratio increased dramatically by 10-16 in both pre-dams due to the removals of proteins and carbohydrates (Appendix, Figure 1), further confirming the predominance of proteins over carbohydrates. Therefore, the down-core variations with respect to the contents of HCl extractable OC and N reflect largely the degradation trend of proteins. Overall, the distribution of hot water extractable proteins does not show a clear relationship to sediment depth. A comparatively large amount of water soluble proteins in the surface sediments at the shallow site of Rappbode pre-dam (**Fig. 3.10**) might be an extra input of fresh land plant detritus from the forest.

There is no evidence for an obvious degradation of HCl extractable proteins in sediment cores at the shallow sites of both pre-dams, except a subtle decline in the surface sediments **Fig. 3.10**. At the deep site, by contrast, the fraction of HCl extractable proteins shrank evidently in the upper 14 cm in Rappbode pre-dam and 10 cm in Hassel pre-dam. The decrease in protein contents is caused partly by the preferential degradation of labile algal OM, and partly by a

down-core decline of microbial biomass in the sediments of both pre-dams which has been measured in other work (Christin, 2013; Walter, 2015; Wendt-Potthoff et al., 2014).

Microbial C declined from 71 to 33 mg g^{-1} for Hassel pre-dam and 32 to 19 mg g^{-1} for Rappbode pre-dam in the upper 10 cm sediment layer at the deep site. At the shallow site, it decreased from 24 to 11 mg g^{-1} and 11 to 3 mg g^{-1} in the upper 5 cm sediment layer for Hassel and Rappbode pre-dam, respectively. Microbial C makes up accordingly 66 to 35% and 37 to 24% of total OC at the deep site of Hassel and Rappbode pre-dam. Knowing protein is the major N-containing constituent and composes of approximate 50% of organic matter in most microorganisms (Simon and Azam, 1989), microbial biomass is the main control on the distribution of proteins at least in sediments of the deep sites in both pre-dams. It should be pointed out that the contribution of microbial biomass to sedimentary OM varies largely to study site as it can be large (Danovaro et al., 1993) or negligible (Hartgers et al., 1994), so its impact on the degradation of protein can be largely different.

Below the depth of 14 cm for Rappbode pre-dam and 10 cm for Hassel pre-dam, the contents of HCl extractable proteins at the deep sites decreased to similar contents at the shallow sites (Fig. 3.10). It thus assumes that OM in surface sediments at the deep sites containing a considerable amount of aquatic and terrestrial proteins. The aquatic fraction has been rapidly degraded in the upper (10-15 cm) sediment layer while the terrestrial fraction is rather stable after buried in sediments. Protein has long been considered as an active organic component with high bioavailability due to the high sensitivity of amide linkage (Derenne and Largeau, 2001). Nevertheless, it is frequently detected in deep sediments with a noticeable amount in lacustrine and marine environments (Hatcher et al., 2014; Menzel et al., 2015; Mylotte et al., 2016; Wakeham et al., 1997). Regarding the existence and resistance of terrestrial proteins in sediments, it can be attributed to the lack of effective microbes as well as the coarseness of particles at the shallow sites and in the deeper sediment layers (below 10 cm) at the deep sites. It can be also attributed to the fact that the proteins of land plant origin have been incorporated into complex macromolecules (melanoidins) or have been encapsulated by other recalcitrant components, defending them from enzymatic attacks (Hedges and Hare, 1987; Knicker and Hatcher, 1997).

Lipids that oxidized by H_2O_2 and $Na_2S_2O_8$ (but H_2O_2 non-oxidizable) are substantially different in molecular structure. The contents of C and N in $Na_2S_2O_8$ oxidizable lipids can be

obtained by determining the C and N losses after $Na_2S_2O_8$ oxidization. However, the C and N contents in H_2O_2 oxidized lipids are not measurable, as this fraction of lipids has been oxidized simultaneously with lignins.

Both H_2O_2 and $Na_2S_2O_8$ oxidizable lipids consist of terrestrial and aquatic sources. The contents of H_2O_2 oxidizable C and N at the shallow sites of both pre-dams are fairly constant, demonstrating the high recalcitrance of H_2O_2 oxidizable lipids in sediments. By contrast, a substantially larger amount of H_2O_2 oxidizable C and N is detected in the upper 15 cm sediments at the deep sites compared to the shallow sites in both pre-dams (**Fig. 3.9**). Therefore, a larger amount of aquatic lipids, which largely account for the degradation of sedimentary OM, contribute to the sediments in the upper 15 cm at the deep sites. Given the distinct $Na_2S_2O_8$ oxidizable C and N contents between the deep and shallow sites, sediments at the deep sites are likely to contain more $Na_2S_2O_8$ oxidizable lipids of aquatic origin than those at the shallow sites. Aquatic $Na_2S_2O_8$ oxidizable lipids have been preferentially degraded in the upper 6 cm sediments in Hassel pre-dam but in the upper 16 cm sediments in Rappbode pre-dam. The remaining lipids, which might be of land-plant origin, degrade slowly or become even concentrated throughout the sediment cores in both pre-dams.

The distinctive degradation behaviors between aquatic and terrestrial lipids in sediments have long been noted (Cranwell, 1978; Cranwell et al., 1987; Muri et al., 2004; Robinson et al., 1984) and still have not been well understood. For example, aliphatic moieties are considered to be resistant to degradation by Hatcher et al. (2014) while rather degradable by Fichez (1991). The complex degradability of lipids because of the diverse structures of lipids (Goossens et al., 1989; Meyers, 2003), and the multiple sources in sediments which include land plant debris, algae and bacteria (Chikaraishi and Naraoka, 2005; Kawamura et al., 1987). In addition, the fact of selective degradation of specific groups of lipids further complicates the degradation of various lipids in sediments (Harvey et al., 1986). The results in this work fully demonstrate that the degradation of lipids is determined by the effect of preferential preservation, the diversity of sources and the differences in chemical resistance.

Lignins in sediments were mainly oxidized by H_2O_2 during the fractionation procedure. Similar to H_2O_2 oxidizable lipids, the C and N contents in lignins are not available. Sediments at the shallow site of Rappbode pre-dam have a higher abundance of lignins than the other three

sampling sites. It is evidenced by a greater C content in H_2O_2 oxidized fraction (containing lignins and lipids, **Fig. 3.10a**) and a larger proportion of lignins in sedimentary OM at this site (**Table 3.4**). In view of the virtually constant C and N contents in H_2O_2 oxidized fractions at the shallow sites of both pre-dams, lignins are considered to be a refractory component like land plant-derived lipids in sediments. The degradation of lignins has been found in the watershed (Hedges et al., 1988), water column (Steinberg et al., 1987) and sediments (Benner et al., 1984; Ishiwatari and Uzaki, 1987). Nonetheless, obvious degradation of lignins is not detected in sediments from both pre-dams, probably due to the absence of fungi (main lignin consumer) or degradable lignins such as cinnamyl and syringyl phenols in sediments. Moreover, it is possible that the lignins in both pre-dams have not been buried long enough (less than 60 years) because the degradation of lignins is rather slow in sediments (Hedges et al., 1982).

4.4.2 Degradation of organic components in sediments-evidence from isotope ratio analysis

The C and N contents of sediments (**Fig. 3.4**) show reverse down-core trends with the stable isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$, **Fig. 3.11**), implying that $\delta^{13}C$ and $\delta^{15}N$ document the processes of sedimentary OM degradation. Various organic components that are characterized by different $\delta^{13}C$ and $\delta^{15}N$ values degrade at different rates in sediments and thereby lead to various degrees of isotopic fractionation. Isotopic fractionation can be a consequence of the changes in the contributions of various organic components (Lehmann et al., 2002; Meyers, 1994; Ogrinc et al., 2005), and can be also the consequence of the transformation of an individual component during diagenesis (Petrišič et al., 2017; Spooner et al., 1994). The effect of isotopic fractionation being caused by the former factor is in general more significant than that being caused by the latter factor (Benner et al., 1987; Carstens et al., 2013). Therefore, the alteration of bulk isotopic composition still reflects principally the change in the biomacromolecular composition of the sedimentary OM.

Characterization of the relative carbon stable isotopic composition of various components is difficult in this work, because of the limited isotopic alterations that are caused by the fractionation procedure. Nonetheless, there are still some indications provided by the isotopic characteristics of the obtained OM fractions. Both terrestrial and aquatic proteins and carbohydrates are ^{13}C-enriched components compared to other organic components in sediments,

which is evidenced by the negative alteration of $\delta^{13}C$ value after HCl hydrolysis (**Fig. 3.11a**). In addition, the alteration of $\delta^{13}C$ value is more evident below the surface sediments at the deep site of Hassel pre-dam and below the depth of 10 cm at the deep site of Rappbode pre-dam. The distinctive alterations of $\delta^{13}C$ value between the upper and deeper sediment layers can be interpreted by the fact that proteins and carbohydrates of terrestrial origin are richer in ^{13}C than those of aquatic origin. Moreover, microbial reworking, which causes positive alteration of $\delta^{13}C$ value with the ongoing OM degradation processes as explained by Hayes (1993) and Keil and Fogel (2001), can be an alternative interpretation.

In the sediments of both pre-dams, the removals of H_2O_2 oxidizable lignins and lipids resulted in negative alterations of $\delta^{13}C$ value in the upper 4cm (at the shallow sites) or 14 cm (at the deep sites) layers while caused positive alterations of $\delta^{13}C$ value below these layers. It thus hypothesizes that the negative alterations are due to the loss of aquatic lipids, since the aquatic fraction of lipids is probably ^{13}C-enriched relative to lignins and terrestrial lipids. Lignin is a ^{13}C-depleted component in original bulk sediments (Benner et al., 1987). However, lignins are presumably richer in ^{13}C than terrestrial lipids in this study, being demonstrated by the more negative alteration of $\delta^{13}C$ value with the decrease of lignin proportion in sediment cores (**Fig. 3.11a**). Since the fraction of lipids, which is resistant to H_2O_2 but is removable by $Na_2S_2O_8$, is substantially more depleted in ^{13}C in the upper 10 cm (Rappbode) or 6 cm (Hassel) sediments, the aquatic $Na_2S_2O_8$ removable lipids are thus considered to be ^{13}C-depleted compared to the other organic components. This depletion of ^{13}C in lipids is supported by Belt et al. (2008) who measures the $\delta^{13}C$ value of lipids by gas chromatography combustion isotope ratio mass spectrometry (GC/C/IRMS). Despite terrestrial OM has greater $\delta^{13}C$ value than aquatic OM, the $\delta^{13}C$ value of terrestrial lipids that are oxidized by $Na_2S_2O_8$ is small than the original bulk sediments in Rappbode pre-dam and is comparable with that of the original bulk sediments in Hassel pre-dam. The different $\delta^{13}C$ values between H_2O_2 and $Na_2S_2O_8$ oxidized lipids might be related to the diverse chemical structures in lipids, which has been published in numerous studies (Canuel et al., 1997; Hayes, 1993; Petrišič et al., 2017; Tolosa et al., 2013).

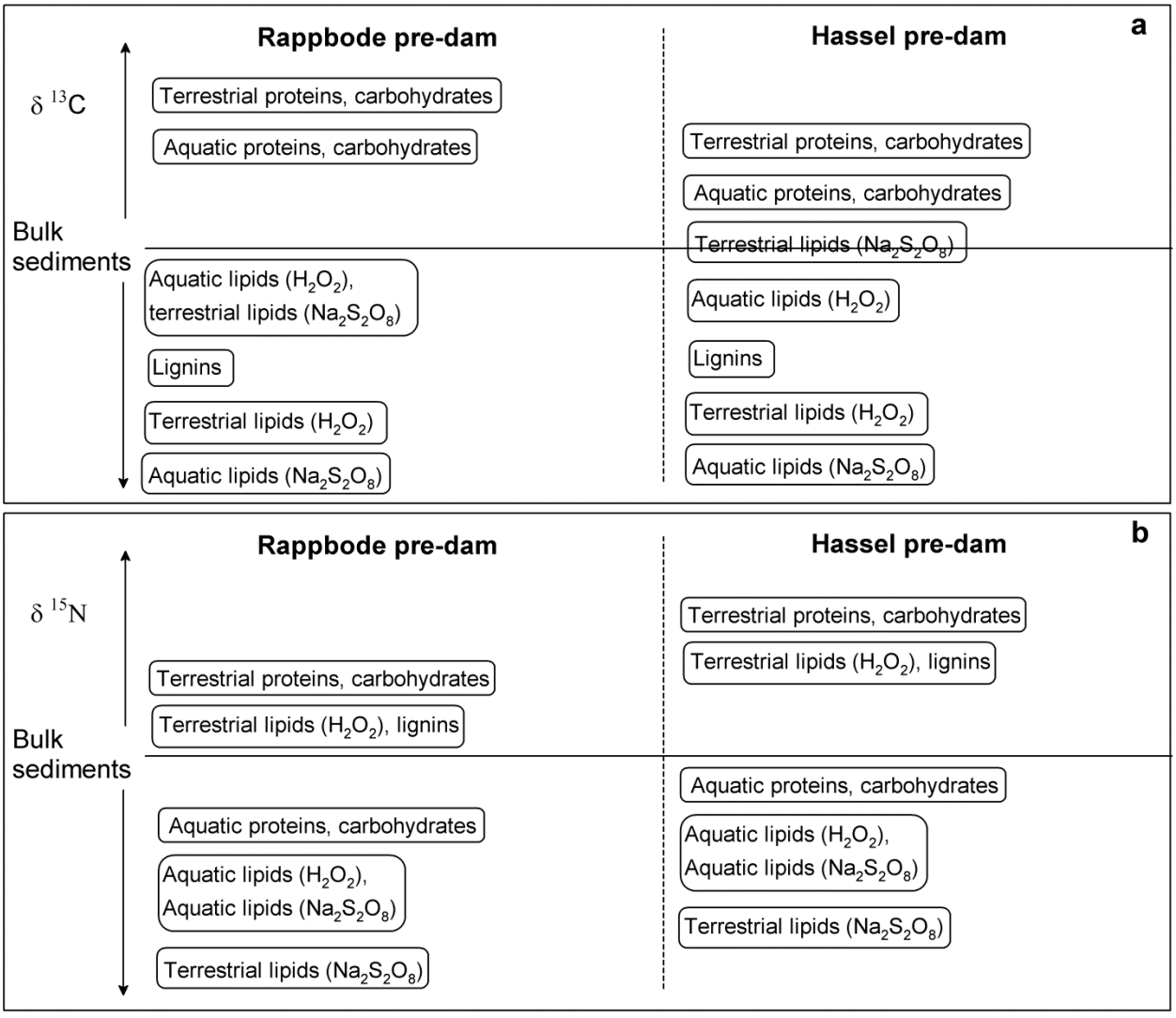


Fig. 4.3 Comparison of (**a**) $\delta^{13}C$ and (**b**) $\delta^{15}N$ values among organic components in bulk sediments as deduced from the fractionation results. Positions of the fields for the single biomacromolecular components reflect the relative increase (heavier) or decrease (lighter) of the isotope ratio compared to the respective isotope ratio of the bulk sediments.

Proteins and carbohydrates in sediments of aquatic and terrestrial origins are distinct in nitrogen stable isotopic composition. Given the relatively less C and N losses (**Fig. 3.10**) but more negative alterations of $\delta^{15}N$ after the HCl hydrolysis in shallow site sediments (**Fig. 3.11b**), proteins and carbohydrates with aquatic sources are isotopically lighter than those derived from the catchment in this region. Moreover, the $\delta^{15}N$ value of bulk sediments ranges between the aquatic and terrestrial proteins and carbohydrates. Similar observations were published by

Batista et al. (2014), who analyzed HCl extracted amino acids with GC-MS and found that most amino acids in algae were more ^{15}N-depleted than in sinking POM and sediments.

Probably due to the different land use in the catchments, lipids and lignins from Hassel catchment have greater $\delta^{15}N$ values than those from Rappbode catchment, which has been indicated by the greater $\delta^{15}N$ alterations during H_2O_2 oxidation. More negative alterations of $\delta^{15}N$ are also observed in sediments below the depth of 4 cm (shallow sites) or 8 cm (deep sites) compared to the sediments above this depth (**Fig. 3.11b**). It points to the smaller $\delta^{15}N$ values in aquatic lipids than in bulk sediments as well as the greater $\delta^{15}N$ values in lignins and lipids that derive from land plants compared to bulk sediments. Terrestrial lipids seem to be not isotopically distinguishable from lignins as no significant difference in $\delta^{15}N$ alterations is detected between the deep (below the depth of 8 cm) and shallow sites in both pre-dams. Lipids that are oxidizable by $Na_2S_2O_8$ are more depleted in ^{15}N than those are oxidizable by H_2O_2, of which, the aquatic fraction of $Na_2S_2O_8$ oxidizable lipids has greater $\delta^{15}N$ value than the terrestrial fraction. These predictions on the lighter $\delta^{15}N$ values of aquatic organic components are in accordance with the relatively small $\delta^{15}N$ values of algae (suspended POM) at the deep sites of both pre-dams (**Fig. 3.3**).

An overall comparison of stable isotopic compositions of various organic components is given in **Fig. 4.3**.

4.4.3 Vertical pattern of sedimentary organic matter degradation

A comprehensive understanding of sedimentary OM degradation is synthesized on the basis of elemental and isotopic analyses of various chemical fractions. Moreover, some critical processes involved in the degradation in sediments are discussed.

Proteins, carbohydrates and lipids of algal origin have been preferentially consumed by bacteria in the upper 4 cm sediments at the deep site of Rappbode pre-dam. Furthermore, at the deep site, the amounts of microbial proteins and carbohydrates have been decreased in the upper 10 cm sediments with the decline of microbial biomass, whereas the microbial lipids have been degraded from the depth of 8 cm to 20 cm. Below this layer, the degradation of OM is attributed to the degradation of lipids and probably lignins with land plant origin. The degradation process could be traced by the alterations of stable isotope ratios of bulk sediments. The ^{15}N-depleted

aquatic OM has been degraded in the upper 20 cm sediments and thereby have given rise to the enrichment of ^{15}N (**Fig. 3.11b**). Aquatic proteins and carbohydrates are comparatively rich in ^{13}C while lipids are depleted in ^{13}C. Therefore, the $\delta^{13}C$ value of bulk sediments has increased only slightly in upper 10 cm sediments that are enriched in aquatic OM enriched and increased rapidly in the layer of 10-20 cm where aquatic OM has been largely reduced. As the isotopically heavy components have been degraded in the upper 20 cm, the loss of terrestrial OM below the depth of 20 cm has not significantly altered the $\delta^{13}C$ value of bulk sediments.

OM degradation pattern at the deep site of Hassel pre-dam differs from that of Rappbode pre-dam. Hot water extractable (microbial) proteins and carbohydrates have been consumed in the upper 4-6 cm sediment layer, whereas more proteins, carbohydrates and lipids of algal origin have accumulated in this layer (**Fig. 3.10**). Therefore, it corresponds to the increase of bulk $\delta^{13}C$ value and the decrease of $\delta^{15}N$ value in this layer. The degradation of microbial proteins, carbohydrates and lipids (HCl extractable) is then detected in the layer of 6-10 cm, which is accompanied by the enrichment of ^{13}C and ^{15}N in bulk sediments. In the layer of 10-16 cm, it seems that only aquatic lipids have been degraded. Since aquatic lipids are isotopically similar to the bulk stable isotopic compositions (**Fig. 4.3**), their degradation has not caused apparent enrichment of ^{13}C. Besides, the degradation of terrestrial lipids and lignins below 16 cm has virtually no effect on the $\delta^{13}C$ value of bulk sediments.

The degradation of OM at the shallow site of Rappbode pre-dam mainly takes place in the top 2 cm sediments, which is in part attributed to the consumption of aquatic proteins, carbohydrates and lipids. Particularly, sediments at this shallow site have had an additional loss of actively terrestrial proteins and carbohydrates (hot water extractable) in the top 2 cm sediments, because the shallow site is located near the inlet of allochthonous input from the forest-dominated catchment. Although the degradation of $Na_2S_2O_8$ oxidizable lipids continues until the deepest point of sediment core (revealed by the enrichment of ^{15}N), the corresponding reduction of OC contents is rather limited. An oddly low amount of $Na_2S_2O_8$ oxidizable lipids at the depth of 4-6 cm is worth to point out (**Fig. 3.10**). It could be related to the turning point in the profile of $\delta^{15}N$ value at the same depth (**Fig. 3.11**), indicating that $\delta^{15}N$ value could be employed as an effective indicator for sedimentary OM degradation.

Table 4.2 Degradation of organic matter in sediment cores: biomacromolecular components which are preferentially degraded in the respective sediment depth

Sediment layer (cm)	Rappbode		Hassel	
	Deep	Shallow	Deep	Shallow
0-2	Algal proteins, carbohydrates and lipids ($Na_2S_2O_8$ oxidizable)	Labile terrestrial, microbial or algal proteins and carbohydrates; algal lipids ($Na_2S_2O_8$ oxidizable)	NA	NND
2-4	Algal proteins, carbohydrates and lipids ($Na_2S_2O_8$ oxidizable)	NND	NND	NND
4-6	Algal proteins, carbohydrates and lipids ($Na_2S_2O_8$ oxidizable)	Algal lipids ($Na_2S_2O_8$ oxidizable)	Microbial proteins, carbohydrates and lipids ($Na_2S_2O_8$ oxidizable)	NND
6-8	Algal and microbial proteins, carbohydrates, lipids (H_2O_2 and $Na_2S_2O_8$ oxidizable)	NND	Microbial proteins, carbohydrates and lipids ($Na_2S_2O_8$ oxidizable)	Algal or microbial proteins, carbohydrates and lipids ($Na_2S_2O_8$ oxidizable)
8-10	Microbial proteins, carbohydrates, lipids (H_2O_2 and $Na_2S_2O_8$ oxidizable)	NND	Microbial proteins, carbohydrates and lipids ($Na_2S_2O_8$ oxidizable)	Aquatic and terrestrial lipids (H_2O_2 and $Na_2S_2O_8$ oxidizable)
10-16	Microbial lipids (H_2O_2 and $Na_2S_2O_8$ oxidizable)	NND	Microbial lipids (H_2O_2 and $Na_2S_2O_8$ oxidizable)	Aquatic and terrestrial lipids (H_2O_2 and $Na_2S_2O_8$ oxidizable)
16-20	Microbial lipids (H_2O_2 and $Na_2S_2O_8$ oxidizable)	NND	Terrestrial lignins and lipids (H_2O_2 and $Na_2S_2O_8$ oxidizable)	NND
20-29	Terrestrial lignins and lipids (H_2O_2 and $Na_2S_2O_8$ oxidizable)	NA	Terrestrial lignins and lipids (H_2O_2 and $Na_2S_2O_8$ oxidizable)	NA

NND= No noticeable degradation.

NA= No sediments available in this layer.

Unlike Rappbode pre-dam, significant degradation of OM occurs only below the depth of 6 cm in sediment core at the shallow site of Hassel pre-dam. It has first started with aquatic proteins, carbohydrates and lipids ($Na_2S_2O_8$ oxidizable) in 6-8 cm layer and has been followed by gradual reduction of aquatic H_2O_2 oxidizable lipids and terrestrial $Na_2S_2O_8$ oxidizable lipids until the depth of 16 cm. Hence, slight enrichment of ^{13}C and ^{15}N are observed. Processes of OM degradation in Hassel and Rappbode pre-dams are summarized in **Table 4.2**.

The reduction of aquatic OM is proposed to be the crucial process for the degradation of OM at the shallow and deep sites in both pre-dams. It is also clear that proteins, carbohydrates and lipids in algal debris, as well as active land plant-derived proteins and carbohydrates are the most degradable OM fractions. Microbial proteins and carbohydrates are then selectively degraded, and microbial lipids are only degraded when proteins and carbohydrates are less available. Nonetheless, the degradation of OM in sediments is largely determined by aquatic lipids due to the limited abundance of aquatic proteins and carbohydrates. It is in good accordance with previous findings that aquatic lipids particularly bacterial lipids is a highly degradable component (Fabiano and Danovaro, 1994; Prahl et al., 1980). In addition, these lipids are predominant fatty acids and usually unsaturated and with short chain length (Kawamura et al., 1987; Meyers et al., 1995).

Concerning the alteration of stable isotopic compositions in sediments, it largely depends on the stable isotopic compositions of primary products in the water column as well as the differences of stable isotopic compositions of diverse organic components. Enrichments of ^{13}C and ^{15}N in sediment cores in both pre-dams are more likely to be the consequence of the loss of isotopically depleted algal derived OM, which is in line with the observations that reported in the modern sediments (Freudenthal et al., 2001; Teranes and Bernasconi, 2000; Vaalgamaa et al., 2013). However, the extent of isotopic composition alteration is also controlled greatly by the respective isotopic compositions of proteins, carbohydrates and lipids.

4.5 Controls on the accumulation and degradation of organic matter in sediments

Differences in terms of OM sources, biomacromolecular compositions and vertical distribution profiles of OM are detected between Hassel and Rappbode pre-dam as well as between deep and shallow sites. There are many factors lead to these differences, among which

two main controlling factors, land use in the catchment and basin topography, are the focuses of this section.

Land use in the catchment is supposed to be a crucial control on the sources and biogeochemical processes of OM in sediments through exerting influences on the primary productivity (Botrel et al., 2014), allochthonous OM (Stallard, 1998), planktonic community and microbial activities in the water column and sediments (Friese et al., 2014; Lake et al., 2000; Wendt-Potthoff et al., 2014). For instance, microbial activities determine to a large extent whether an organic compound can be effectively and rapidly degraded. Besides, the susceptibility to degradation and biomacromolecular composition of sedimentary OM represent its bioavailability to microbes. In consequence, land use in the catchment affects the proportions of terrestrial and aquatic OM and OM degradation environments, such as light, pH, redox condition, temperature, and eventually influences the quality and quantity of sedimentary OM (Arndt et al., 2013). Catchment area to surface water area ratio and soil types could additionally complicate the assessment of the influences of land use (Knoll et al. 2003). The similarities in morphology, water capacity and catchment size between these two pre-dams imply that the dominance of agricultural land use in Hassel catchment and the dominance of forest (almost no agricultural land) in Rappbode is an essential attribution for the different aquatic contributions to sedimentary OM.

The high forest coverage in the catchment of Rappbode pre-dam might play a critical role in the composition of terrestrial and aquatic sources in sedimentary OM. In addition, ^{13}C NMR analysis demonstrates that the forest in the catchment can increase the aromaticity of OM. A similar finding was obtained through a measurement with FTICR-MS (Fourier Transform Ion Cyclotron Resonance-Mass Spectrometer) which was carried out on the DOM in the same pre-dam (Raeke et al., 2017). It can be explained by the comparatively high recalcitrance and mobility of organic compounds in plant remnants which are ultimately washed into pre-dam. It can be instead explained from the quantitative perspective that a larger amount of allochthonous DOM has been discharged into the mesotrophic Rappbode pre-dam (Friese et al., 2014). It implies that more allochthonous POM could be achieved via flocculation in the water column (von Wachenfeldt et al., 2008). The agriculture land in the catchment of Hassel pre-dam is considered to be a major attribution for the high aliphatic property and the predominance of

aquatic OM sources in sediments, which might be related to the greater primary productivity and sedimentation rate in Hassel pre-dam.

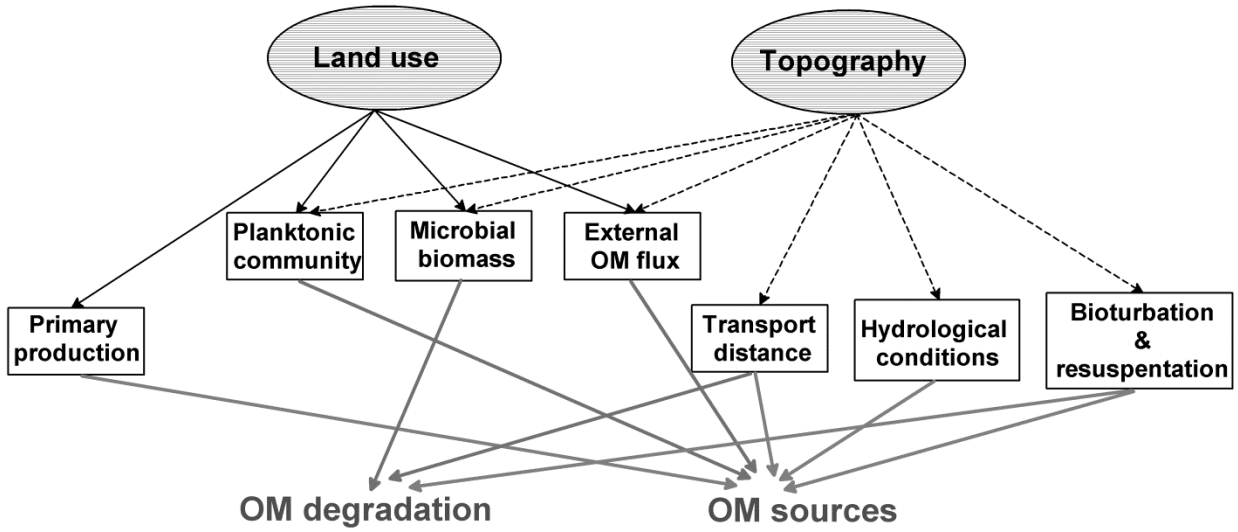


Fig. 4.4 Illustration of the controls of land use type in the catchment and topography of water basin on the accumulation and degradation of OM in sediments.

Land use in the catchment is at least an indirect driver for the distinct patterns of sedimentary OM degradation in Hassel and Rappbode pre-dam. The intensive degradation of sedimentary OM in Hassel pre-dam (e.g. TOC degraded on average 3.1 mg g^{-1} cm^{-1} at the deep site) started taking place in a sediment layer which is 4-6 cm deeper than that in Rappbode pre-dam. This difference might be a consequence of the high C and N sedimentation rate in Hassel pre-dam. Sediment trap study has indicated the higher C and N contents in sinking POM in Hassel pre-dam and particularly at the deep site (**Fig. 3.1**). It demonstrated that the fresh algae-derived OM depositing in the upper 0-4 cm sediments is able to compensate the loss of OM due to the microbial decomposition. However, this process has not been fully revealed, and further investigation is still required for a better understanding of the 'lagging' degradation of OM in the upper sediment layer in this eutrophic water basin. Nonetheless, the rapid degradation of OM below this layer in Hassel pre-dam can be well explained by a greater microbial biomass in sediments which has been previously detected at the same sites by Wendt-Potthoff et al. (2014).

Another controlling factor, basin topography, is revealed by comparing the properties of sedimentary OM between the deep and shallow sites within two pre-dams. Due to the construction of pre-dam, the shallow site is generally near the inflow while the deep site is lake

like. In consequence, the primary production and OM sedimentation at the shallow site differ from the deep site. Based on the review of Kimmel and Groeger (1984), there are three explanations for a lower primary productivity at the shallow site: 1) lower light availability at the shallow site that is caused by a higher turbidity of water; 2) nutrients are less available at the shallow site because of a higher flow velocity; 3) the water column at the shallow site has less stable stratification, which obstructs the growth of algae. Generally, a larger amount of terrestrial POM settles at the shallow site, whereas the finer terrestrial and aquatic POM is forced to move forward and deposit at the bottom of the deep site. POM at the shallow site also benefits from a shorter lateral transport distance and gravitational sinking depth, which shortens the exposure time to oxygen and biochemical transformation (Hartnett et al., 1998). However, the active resuspension and bioturbation at the shallow site may promote the oxidation and biological reworking of the fine and labile portion of POM.

Interpretation of the distinct degradation patterns of sedimentary OM between the deep and shallow sites in a pre-dam is even more challenging. Lateral transport of sediments along the slope occurs especially with the presence of intense bottom water current. Therefore, the surface sediments at the deep site are a mixture of buried sediments from the shallow site and fresh sediments from the overlying water column. Further degradation of OM can be expected in sediments during lateral transport. The shallow site has been resupplied by newly deposited sediments before OM degradation could take place, which interprets partly the low degradation extent of sedimentary OM at the shallow site.

Terrestrial OM has undergone intensive biochemical reworking before the arrival to the water basin. It leads to the relatively low bioavailability (i.e., the selective preservation) of a terrestrial fraction of sedimentary OM relative to the aquatic fraction (Guillemette et al., 2017). The low bioavailability of terrestrial OM causes partly the smaller microbial biomass in the sediments (Danovaro et al., 1993; Mincks et al., 2005) and further slows the degradation of sedimentary OM degradation at the shallow site. Comparing the biomacromolecular compositions of OM between the deep and shallow sites provides an evidence of the relatively passive OM degradation at the shallow site. The observation based on the ^{13}C NMR analysis indicates that sedimentary OM at the shallow site is dominated by more unpalatable components (e.g. aromatic compounds like lignins) compared to that at the deep site. Instead, the steady

hydrological and biochemical environments at the deep site provide proper conditions for the growth of bacteria, which play a critical role in the consumption of buried OM in sediments. Moreover, the finer fraction of sediments at the deep site also promotes significantly the efficiency of OM degradation by increasing the accessibility of bacteria to organic food in sediments.

Chapter 5 Concluding remarks and future directions

This thesis studies the biogeochemistry of sedimentary OM in two modern freshwater bodies (Hassel and Rappbode pre-dam) with contrasting catchment land use with respect to the OM sources and degradation processes in sediments.

A new concept of was developed employing a stepwise fractionation to quantify a range of OM fractions in sediments in terms of their biomacromolecular composition. The sequential fractionation method was able to quantify more than 95% of TOC and TN in bulk sediments. Previously, only known organic compounds were extracted separately, leading to a percentage of 20-80% for identifiable sedimentary OM (Arndt et al., 2013; Burdige, 2007; Hatcher et al., 1982; Hatcher et al., 1983). Identifying the biomacromolecular organic components has a profound implication. Combined characterizations of the isolated OM fractions by ^{13}C NMR spectroscopy and EA-IRMS reveal the correlation between the biomacromolecular and stable isotopic compositions. This correlation can further promote the application of stable isotope ratios in tracing OM degradation in sediments.

Sediment trap material indicates that sedimentary OM depends on the aquatic sources to varying degrees in Hassel and Rappbode pre-dam. As revealed by the seasonal changes of C/N ratio and $\delta^{13}C$ and $\delta^{15}N$ values in sinking POM, the aquatic OM plays a more important role in the accumulation of OM in Hassel pre-dam, whereas terrestrial OM is more dominant in Rappbode per-dam. The contribution of aquatic and terrestrial sources to sinking POM in Hassel pre-dam varies more significantly with water depth than in Rappbode pre-dam. Sediment trap data also reflect that C/N ratio and $\delta^{15}N$ values give clearer indications to the degradation of POM and the change of phytoplankton productivity in the water column as $\delta^{13}C$ values do.

The down-core variations of the biogeochemical proxies can be used for identifying the relative importance of aquatic and terrestrial OM in sediments as well as for gaining a systematic insight of the degradation processes of OM. Comparisons of biomacromolecular compositions, C/N ratios, $\delta^{13}C$ and $\delta^{15}N$ values of OM fractions between both pre-dams, between the deep and shallow sites of each pre-dam and throughout the different depths in the sediment cores provide valuable information. A predominance of terrestrial OM is observed in the sediments at the shallow site of Rappbode pre-dam and below the sediment depth of 10 cm at the shallow site of

Hassel pre-dam. The proportions of terrestrial OM at the deep sites of both pre-dams increase with sediment depth, indicating that aquatic OM is preferentially consumed by bacteria. Furthermore, the distribution of proteins, carbohydrates, lignins and lipids in sediments has been identified. Therefore the degradation of OM at different depth can be assigned to the loss of one or more specific organic components. These findings provide direct evidence of the selective degradation of proteins and carbohydrates of aquatic origins, followed by aquatic lipids when proteins and carbohydrates are less available. Conversely, terrestrial OM is stable in sediments and makes up a substantial part of the carbon sink in aquatic ecosystems.

Implications from this work can be further drawn in the application of stable isotopes analyses and the clarification of critical controls on OM production and degradation in the water column and sediments. The findings of this study demonstrated that carbon and nitrogen stable isotopic compositions of sediments are greatly determined by the dominant sources of OM, and also are regulated by the biomacromolecular composition of sedimentary OM. Moreover, these observations emphasized the influences of land use in the catchment and bottom topography of the water bodies for the quantity and quality of OM before and after its deposition in the sediments.

The establishment of the sequential fractionation method and the combination of ^{13}C NMR and stable isotopic composition analyses clarify the degradation processes of sedimentary OM. The findings of this work illustrated the significance of the separation of OM in terms of its aquatic and terrestrial sources and its biomacromolecular composition due to their different fates in sediments. Hence, this work could refine the calculation of carbon budget by taking the different degradability of organic components of various sources into consideration. The methodology is not geographically limited and can be used for the investigations on the sedimentary OM in other freshwater and marine ecosystems.

Although this work provides a more integrated and specified pattern about the distribution and degradation of OM in sediments, open questions still remain. One aspect which could be improved in future work is the interpretation of the distinct degrees of degradation between terrestrial and aquatic proteins, considering the considerable and stable amount of proteins in the deep layer of sediments. A closer look at the sedimentary proteins of various origins, such as a solvent extraction of amino acids, could lead to a deeper understanding about the persistence of

proteins in sediments. Moreover, an isolation of lignins from lipids is suggested if comparisons between deep and shallow sites within a water body are impracticable at other study sites. Further work would also benefit greatly from a separation of microbial and algal OM, since algae and microbes are two main donors to the labile fraction of sedimentary OM. A promising approach might be differentiating both donors on the basis of the distinct nitrogen stable isotopic compositions. To gain more knowledge on the dynamics of sediments, radiocarbon dating is required especially when there is a movement of sediments from the shallow site to the deep site. In addition to further steps in this line of research, conjunct characterizations of OM with multiple techniques are highly recommended. For instance, a combination of measures (e.g. CSIA and FTIR) can largely facilitate the interpretation of the biogeochemistry of OM in aquatic ecosystems by providing information at a molecular level.

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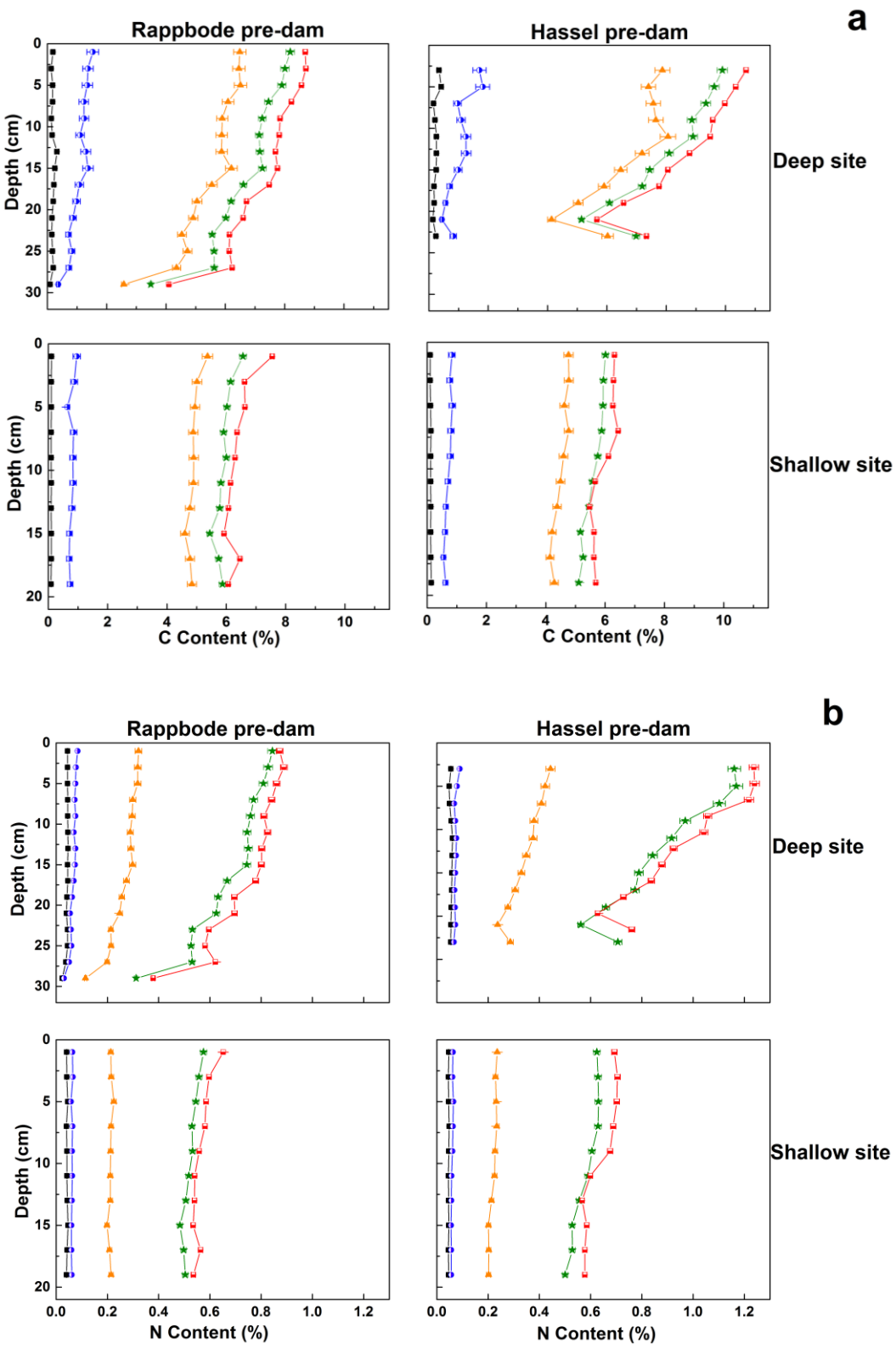
Appendix


a
Rappbode pre-dam
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N Content (%)

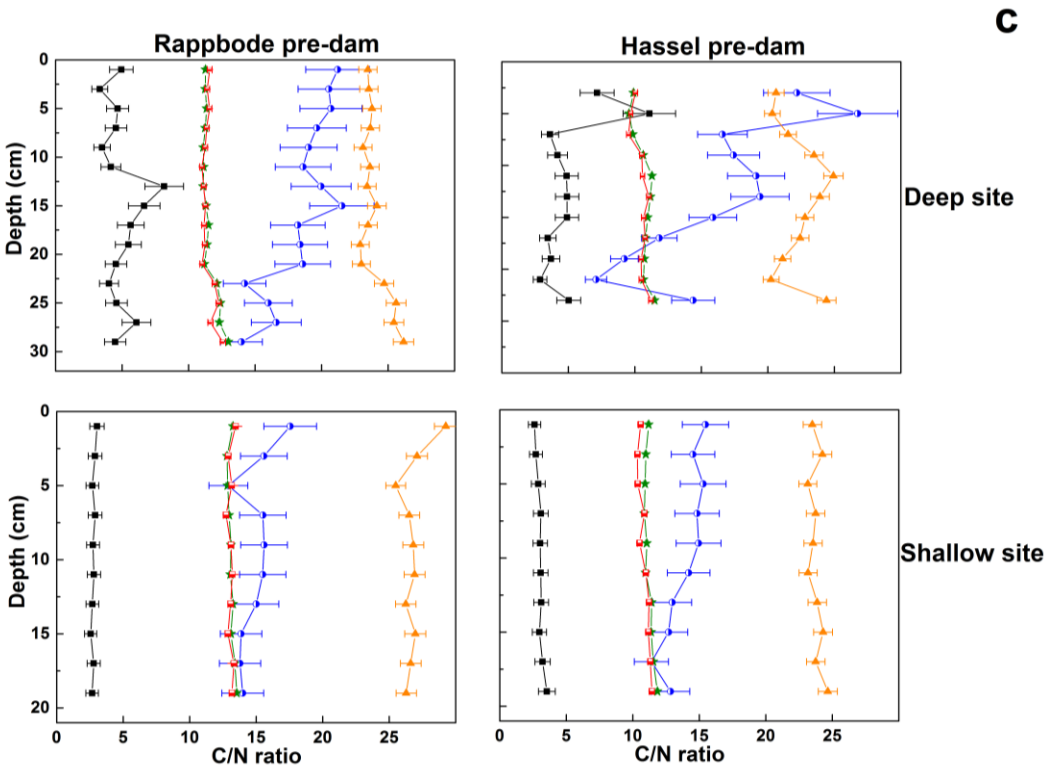

Figure 1 C (**a**), N (**b**) and C/N ratio (**c**) of bulk samples and chemical resistant residues obtained from sediment cores. Sediments were sampled from cores at the deep and shallow sites of Rappbode and Hassel pre-dams. Red line with half-open square symbols represent original bulk sediments; Green line with star symbols represent hot water resistant residue; Orange triangle symbol represent HCl resistant residue; Purple half-open circular symbols represent H_2O_2 resistant residue; Black solid square symbols represent $Na_2S_2O_8$ resistant residue. Error bars for standard deviations were calculated from three replicates. For samples without replicates, standard deviations were calculated from the deviation rate in each sediment core (see Chapter 2.5 and Fig. 2.2).

Table 1 Relative distribution of C functional groups (in percentage) in HCl and H_2O_2 resistant residues in sediment core study. Data are integration results of ^{13}C NMR spectra

Functional group	Deep-Hassel (%)		Shallow-Hassel (%)		Deep-Rappbode (%)		Shallow-Rappbode (%)	
	HCl	H_2O_2	HCl	H_2O_2	HCl	H_2O_2	HCl	H_2O_2
Alkyl C	52.92	70.83	47.73	72.80	50.72	73.41	38.86	75.89
N-alkyl C	4.97	4.12	5.04	0.66	3.40	3.28	7.36	1.92
O-alkyl C	8.20	4.76	8.08	5.36	8.76	4.38	9.57	6.04
O_2-alkyl C	3.89	4.85	1.72	1.87	2.24	2.57	2.53	1.47
Aromatic C	13.40	5.37	20.18	7.95	18.79	6.65	24.52	6.41
O-aromatic C	6.06	3.33	8.80	4.34	8.50	2.56	7.17	1.79
Carboxyl C	10.57	6.74	8.44	7.02	7.59	7.15	9.97	6.49

Table 2 Sedimentation rate in Hassel and Rappbode pre-dams in 2016

Sampling date	Hassel (mg m^{-2} d^{-1})			Rappbode (mg m^{-2} d^{-1})		
	Shallow (4 m b.w.)[a]	Deep (6 m)	Deep (2 m a.b.)[b]	Shallow (4 m b.w.)[a]	Deep (6 m)	Deep (2 m a.b.)[b]
23.03.2016	5.52	NA	6.40	7.76	5.73	6.33
21.04.2016	5.66	5.04	4.45	7.76	5.97	7.53
26.05.2016	4.68	4.68	5.97	NA	5.50	6.64
23.06.2016	8.11	4.81	4.95	5.24	59.36	6.48
20.07.2016	7.38	6.41	4.37	4.72	5.97	7.96
11.08.2016	8.41	4.68	7.95	7.97	6.32	6.04
15.09.2016	6.27	6.13	4.44	5.62	12.73	9.50
12.10.2016	8.73	65.70	8.82	7.24	8.22	8.65
10.11.2016	6.91	6.64	8.34	5.73	5.75	7.53
15.12.2016	NA	6.48	7.09	NA	6.11	12.70

[a] Sediment trap fixed at 4 m below the water surface.

[b] Sediment trap fixed at 2 m above the bottom of water basin.

Curriculum Vitae

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EDUCATION

Oct. 2014- present	Enrolled for a Ph.D. degree at the Faculty of Natural Science at the Martin Luther University of Halle-Wittenberg
Sep. 2011-July 2014	Master in Nuclear Energy and Nuclear Engineering at Sichuan University
Sep. 2006-June 2010	Bachelor in Radiation Protection and Environmental Engineering with a minor in English at East China University of Technology

RESEARCH EXPERIENCE

Oct. 2014- present	**Ph.D. research in Isotope Geochemistry** at the Helmholtz Centre for Environmental Research, with a focus on the biogeochemistry of sedimentary organic matter in freshwater ecosystems. Topic of the doctoral dissertation: "Source identification and specific degradability of particulate and sedimentary organic matter in reservoirs". Supervisor: Prof. Dr. Kurt Friese.
Sep. 2011-July 2014	**Study of Radioactive Chemistry** with particular interest into isotope research and application. Cooperative projects: I. Thermodynamic and kinetic behavior of solvent extraction of U (Ⅵ) and Th (Ⅳ) from nitric acid solution with tri-isoamyl phosphate; II. The efficacy of fullerene derivatives in sequestering ^{238}U and ^{153}Sm in mice. Supervisor: Prof. Ning Liu.
Mar. 2010-June 2010	Bachelor thesis: The ultraviolet radiation tolerance of eosinophil uranium leaching microbes. Supervisor: Prof. Yajie Liu.

PROFESSIONAL AFFILIATION

Since Nov, 2016	Association for the Sciences of Limnology and Oceanography (ASLO) member

LIST OF PUBLICATIONS (PEER-REVIEWED)

Liu, X., Y., Yang, Y., J., Liao, J., Ou, W., Kong, F., Lan, J., Luo, S., Liu, G., He, J., Yang, J., Tang, J., Liu, N. 2015. Efficient removal of uranium from mice by a novel compound of fullerene multi-macrocyclic polyamine derivatives. Nuclear Science and Technology 26, 040302 1-6. DOI: 10.13538/j.1001-8042/nst.26.040302

Liu, X., Kong, F., Liao, J., Ding, S., Yang, Y., Huang, H., Luo, S., Liu, G., He, J., Yang, J., Tang, J., Liu, N. 2014. Extract-ion kinetics of Uranium (VI) and Thorium (IV) with Tri-iso-amyl phosphate from nitric acid using a Lewis Cell. Journal of Radioanalytical and Nuclear Chemistry 302:1069–1076. DOI: 10.1007/s1 0967-014-3447-9

Liu, X., Hilfert, L., Rinke, K., Friese, K.. Stable isotope ratio and ^{13}C NMR analyses confirm sedimentary organic matter pools of increasing structural simplicity and recalcitrance (under review by Biogeochemistry).

Liu, X., Wendt-Potthoff, L., Hilfert, L., Rinke, K., Friese, K.. Sedimentary organic matter stabilization and degradation in two pre-dams with different land use catchments (will be submitted in Nov, 2017).

ACADEMIC ACTIVITIES

Feb. 2017	**Liu, X.**, Friese, K., Rinke, K.. Sedimentary organic matter in two pre-dams with different land-use in their catchments. Aquatic Science Meeting (ASLO), oral presentation. Honolulu, Hawai'i, U.S.A.
Sep. 2016	**Liu, X.**, Friese, K., Rinke, K.. Organic carbon pools fractionation of lacustrine sediments with a stepwise chemical procedure. International Conference on Isotope Hydrology and Geochemistry, oral presentation. Rome, Italy
Sep. 2016	**Liu, X.**, Friese, K., Rinke, K.. Carbon pools fractionation of sediment from two pre-dams of a drinking water reservoir. HIGRADE Fall Conference, poster presentation. Leipzig, Germany.

AWARDS AND HONORS

Oct, 2013	Prize for an oral presentation during the 2013 Isotope Academic Seminar of Nuclear Society (third place)
June, 2010	Cum laude graduate of East China University of Technology
Dec, 2009	Third place for the Student Technological Creative Project (STCP) "A survey of the impacts of radioactive wastewater disposal on environment"

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Eidesstattliche Erklärung/ Declaration under Oath

Ich erkläre an Eides statt, dass ich die Arbeit selbstständig und ohne fremde Hilfe verfasst, keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt und die den benutzten Werken wörtlich oder inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.

I declare under penalty of perjury that this thesis is my own work entirely and has been written without any help from other people. I used only the sources mentioned and included all the citations correctly both in word or content.

09.11.2017 Xiaoqing Liu

Datum/ Date Unterschrift des Antragstellers/ Signature of the applicant