Role of the sediments for dissolved organic carbon (DOC) in drinking water reservoirs

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Gutachter:

1. Prof. Dr. Kurt Friese

   Helmholtz-Zentrum für Umweltforschung - UFZ, Department Seenforschung

2. Prof. Dr. Herbert Pöllmann

   Martin-Luther-Universität Halle-Wittenberg, Institut für Geowissenschaften und Geographie

3. Prof. Dr. Harald Biester

   Technische Universität Braunschweig, Institut für Geoökologie

Tag der Verteidigung:

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Dedication

To my late parents for the inspiration.

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Summary

Dissolved organic carbon (DOC) brownification of surface waters in the northern hemisphere is increasing and poses social, ecological, and health problems. Processes and drivers leading to the increasing DOC trend are not yet fully revealed and understood, despite various hypotheses having been put forward. One wonders what role the lake and reservoir sediments play in DOC exchange, considering that the sediment water interface is the most dynamic and reactive part of the aquatic system.

This thesis details an investigation of benthic DOC exchange in three drinking water reservoir pre-dams by focusing on fluxes, processes and drivers. The benthic systems were intensively studied through a combination of batch sediment core incubation, microbiological (Biolog EcoPlates) and DOC quality (FTICR-MS) methods. This was done through quantification of seasonal benthic DOC, nitrogen, phosphorus, iron, manganese, sulphate, and methane fluxes (incubation and resuspension), determination of metabolic potentials, and determination of molecular composition of DOC. The combination of seasonal and multi-solute data enabled elucidation of major drivers and mechanism regulating DOC flux.

Identification and modification of a suitable method to quantify DOC and other solutes fluxes was important for this work, hence a batch core sediment incubation method was developed. The method enables successful solute flux measurements, within 14 days, under both oxic and anoxic conditions with ability to separate measurement of fast and slow fluxes. Furthermore analysis of minimal sample volume (2% of overlying water) is possible thereby countering negative effects of withdrawal of large sample volumes from the cores. The correlation between ultraviolet absorption at 254 nm and DOC concentration was very strong in oxic waters; however it was very weak in anoxic waters. Therefore, $UV_{254\ nm}$ cannot be used as a proxy for DOC concentration in anoxic waters.

Sediments were a source of DOC under anoxic conditions with fluxes ranging between 0.5 and 5.3 mmol m^{-2} d^{-1}. In contrast, sediments were both a sink and source of DOC under oxic conditions with fluxes ranging between -9.3 and 2.4 mmol m^{-2} d^{-1}. Redox conditions and temperature were identified as the major drivers of benthic DOC exchange.

Sediment resuspension is a relevant process in the pre-dams with a single resuspension event DOC flux being approximately equal to 9-17 days of the diffusive flux. Generally sediments were a sink of DOC after a resuspension under oxic conditions and the opposite being true under anoxic conditions. In addition, nutrient release under oxic conditions was negligible. Sediment resuspension increased the utilization of organic substrates, which can be attributed to introduction of heterotrophic bacteria into the water after resuspension.

There was a strong positive correlation of DOC and Fe fluxes under anoxic conditions and a strong negative correlation under oxic conditions underlining immobilization/mobilization of DOC by Fe minerals as an important mechanism. Interestingly, DOC quality analysis also showed the same results, under anoxic conditions water quality signature was dominated by oxygen rich organic compounds, which disappeared when redox conditions were manipulated to oxic. These compounds are known to be strongly associated with Fe minerals through adsorption under oxic conditions and are desorbed under anoxic conditions following reductive dissolution of Fe minerals. I propose a conceptual model with the redox driven adsorption/desorption of DOC on iron in combination with temperature regulated microbial activities as the major processes regulating benthic DOC exchange.

The DOC budget calculations demonstrates that benthic DOC exchange in the reservoirs studied plays a negligible role in immobilizing/mobilizing DOC compared to DOC input from the catchment. However DOC exchange still remains an important process for in-lake carbon exchange. The role and interaction of redox conditions and temperature on benthic DOC release might be enhanced by the envisaged global warming. This might imply longer and stronger stratification accompanied with anoxia in the future.

There is very little literature on benthic DOC flux measurements, and most of the studies did not cover seasonality effects. The in-depth process and drivers study of benthic DOC and other solutes exchange presented in this thesis is a milestone in availing benthic DOC flux data.

Zusammenfassung

Die zunehmende Konzentration von gelöstem organischem Kohlenstoff (DOC) in zahlreichen Oberflächengewässern verursacht soziale, ökologische und Gesundheits-Probleme. Die für den ansteigenden DOC verantwortlichen Treiber sind nicht vollständig verstanden – verschiedene Erklärungsansätze werden zur Zeit diskutiert. Fast nichts ist darüber bekannt welche Rolle die Sedimente in Seen und Talsperren für den DOC im Wasser spielen, obwohl bekannt ist, dass die Sedimentoberfläche einer der dynamischsten und reaktivsten Bereiche im Gewässer darstellt.

In dieser Dissertation wird der benthische DOC-Austausch in drei Vorsperren von Trinkwassertalsperren untersucht. Der Fokus liegt dabei auf der Quantifizierung von Stoffflüssen und der Identifizierung von den dahinterliegenden Prozessen und Treibern. Dafür wurde eine Kombination verschiedener Methoden angewandt: Sedimentkern-Inkubationen zur Quantifizierung der saisonalen benthischen Flüsse von DOC, Stickstoff, Phosphor, Eisen, Mangan, Sulfat und Methan; mikrobiologische Assays (Biolog EcoPlates) zur Ermittelung des metabolischen Potenzials im Wasser sowie hochauflösende Massenspektrometrie zur Untersuchung der DOC-Qualität. Die Kombination aus saisonalen Daten von DOC und anderen gelösten Stoffen erlaubt die Analyse der wichtigsten Treiber und regulatorischen Mechanismen.

Die Identifizierung und Anpassung einer geeigneten Methode zur Messung benthischer Stoffflüsse war eine wichtige Grundlage für die Arbeit. Als Ergebnis wurde eine Sedimentkern-Inkubationsmethode zur Messung von langsamen und schnellen Stoffflüssen sowohl unter oxischen als auch anoxischen Bedingungen entwickelt. Die Analyse des Überstandswassers wurde auf kleine Probenmengen optimiert, so dass maximal 2% des Wassers ausgetauscht werden mussten und so Probenahmeffekte minimiert waren. Die Korrelation zwischen der spektralen Absorption bei 254 nm (SAK) und der DOC Konzentration war nur unter oxischen Bedingungen signifikant, nicht jedoch unter anoxischen Bedingungen. Deshalb kann der SAK in anoxischem Wasser nicht als Proxy für DOC verwendet werden.

Unter anoxischen Bedingungen waren die Sedimente eine DOC-Quelle mit Flüssen zwischen 0.5 und 5.3 nmol m^{-2} Tag^{-1}. Im Gegensatz dazu waren die Sedimente unter oxischen Bedingungen sowohl eine Quelle als auch eine Senke für DOC mit

Flüssen zwischen -9.3 und 2.4 nmol m^{-2} Tag^{-1}. Redox-Bedingungen und Temperatur wurden als wichtigste Treiber identifiziert.

Die Resuspension von Sediment bewirkte einen verstärkten Austausch von DOC zwischen Sediment und Wasser, wobei ein Resuspensionsereignis äquivalent zu 9-17 Tagen diffusiven Stoffaustausches war. Im Allgemeinen war das Sediment eine DOC Senke bei Resuspension unter oxischen Bedingungen und umgekehrt eine DOC Quelle unter anoxischen Bedingungen. Resuspension hatte demgegenüber einen geringen Effekt auf Nährstofffreisetzungen aus dem Sediment. Resuspension trug heterotrophe Bakterien aus dem Sediment in das überstehende Wasser ein und verstärkte so den hypolimnischen DOC Abbau.

Der Flux von DOC war eng mit dem Flux von Eisen korreliert, was zeigt, dass die Mobilisierung/Immobilisierung von DOC eng an Eisenminerale gekoppelt war. Interessanterweise wird dies durch die Analyse der DOC Qualität unterstützt: Unter anoxischen Bedingungen war der DOC durch sauerstoffreiche Verbindungen dominiert, von denen bekannt ist, dass sie unter oxischen Bedingungen bevorzugt an Fe-Minerale binden bzw. bei der reduktiven Auflösung der Minerale freigesetzt werden. Aufbauend auf diese Beobachtungen wird ein konzeptionelles Modell zum benthischen DOC Austausch vorgestellt, in dem redox-getriebene Adsorption/Desorption von DOC an Eisen in Kombination mit temperaturgesteuerten mikrobiellen Prozessen die wesentlichen Prozesse darstellen.

Die Berechnung von Stoffbilanzen zeigt, dass der benthische DOC-Austausch verglichen mit dem Eintrag aus dem Einzugsgebiet vernachlässigbar war. Für den See-internen Kohlenstoffkreislauf jedoch ist der Austausch von DOC zwischen Sediment und Wasser ein wichtiger Prozess. Es ist zu erwarten, dass es im Zuge des Klimawandels mit höheren Temperaturen und stabilerer Schichtung mit vermehrt anoxischen Bedingungen zu einer Zunahme von benthischer DOC Freisetzung in Seen und Talsperren kommen wird.

Es gab vor dieser Arbeit wenige quantitative und saisonale Informationen über benthische DOC-Flüsse in Seen und Talsperren. Die Aufklärung der beteiligten Prozesse und Treiber in dieser Dissertation bedeuten einen wichtigen Schritt vorwärts im Verständnis des gewässerinternen Kohlenstoffkreislaufes.

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List of acronyms and chemical symbols

AWCD	Average well colour development
C	Carbon
CH_4	Methane
CHO	Carbon, hydrogen, oxygen components
CO_2	Carbon dioxide
DBL	Diffusive boundary layer
DGT	Diffusion gradient in thin films gels
DOC	Dissolved organic carbon. Also used in text to refer to dissolved organic matter
DBP	Disinfection by-product
Fe	Iron
Fe(II)	Ferrous iron
Fe(III)	Ferric iron
FTICR-MS	Fourier transform ion cyclotron resonance mass spectrometry
HAAs	Haloacetic acids
H/C	Hydrogen carbon ratio
LOI	Loss on ignition
NH_4^+	Ammonium
NO_3^-	Nitrate
Mn	Manganese
O/C	Oxygen carbon ratio
$OD_{595\ nm}$	Optical density at 596 nm
OM	Organic matter (OM)
P	Phosphorus
POC	Particulate organic carbon
POM	Particulate organic matter
SO_4^{2-}	Sulphate
SPE	Solid phase extraction
SRP	Soluble reactive phosphorus
$SUVA_{254\ nm}$	Specific ultraviolet absorption at 254 nm
THMs	Trihalomethanes
TIC	Total inorganic carbon
TOC	Total organic carbon
$UV_{254\ nm}$	Ultraviolet absorption at 254 nm

Chapter 1: Introduction

1.1 Motivation

Dissolved organic carbon (DOC) increases and expected increase in surface waters of the northern hemisphere is an emerging issue of concern (Freeman et al. 2001; Evans et al. 2005; Monteith et al. 2007; Couture et al. 2011; Larsen et al. 2011; Laudon et al. 2011). The concern emanates from ecological, health and aesthetic DOC implications. Dissolved organic matter despite being an energy source for heterotrophs is also light absorbing and affects light penetration depth in surface water (Williamson et al. 1996; Maloney et al. 2005; Staehr et al. 2010). Alteration of light penetration can affect primary production and may result in aquatic systems which are net heterotrophic (Del Giorgio et al. 1999; Cole et al. 2000; Hanson et al. 2003; Staehr et al. 2010; Sadro and Melack 2012). Moreover changes in light regimes can result in a higher demand for photo harvesting iron (Fe) in some phytoplankton species, as organisms adjust to low light conditions (Strzepek et al. 2012) leading to preferential selection of some species. For example cyanobacteria may prevail because of their low light requirements (Scheffer et al. 1997; Litchman 2003), and ability to scavenge for Fe from Fe-ligands, which is unavailable to other species (Sorichetti et al. 2016). There are many other ecological quality implications of DOC: greenhouse gas production (Peura et al. 2014), metal availability and speciation (Shafer et al. 1997), influencing acid-base chemistry in aquatic systems (Hruška et al. 2003) and effects on biochemistry of freshwater organisms (Steinberg et al. 2006).

The brown colour of DOC makes it an undesirable component in drinking water. The cost of DOC removal from water by coagulants increases with increasing DOC concentration (Eikebrokk et al. 2004). Furthermore diversity and complexity of

DOC components entails removal by more than one method, creating problems for water treatment plants since they have to optimise their facilities in order to deal with different concentrations and different types of DOC components (Sillanpää 2015). Dissolved organic carbon also leads to frequent fouling (Zhang et al. 2003; Rahman et al. 2014) of filters and hence an increase in maintenance cost for water treatment plants. Furthermore DOC can react with disinfection agents like ozone and chlorine to form disinfection by-products: trihalomethanes (THMs) and haloacetic acids (HAAs) which are potentially harmful to health (Escobar et al. 2001; Galapate et al. 2001; Skrasner et al. 2006; Richardson et al. 2007; Gough et al. 2014). In addition DOC stimulates growth of microbes in distribution systems (Ramseier et al. 2011; Thayanukul et al. 2013), and therefore more disinfection agents than usual are required. Presence of DOC can also result in mobilization of arsenic (Bauer and Blodau 2006), which also have some impacts on human health.

Increasing DOC has been attributed to changes in atmospheric sulphur deposition (Evans et al. 2006; Vuorenmaa et al. 2006), increased atmospheric carbon dioxide (Freeman et al. 2004), and increased nitrogen deposition (Findlay 2005). However the processes and mechanisms behind DOC mobilization within different catchment compartments are not fully understood. One important compartment of a catchment is standing water bodies (lakes and reservoirs). The role of lakes cannot be overemphasized; global lake areas are > 3% of the continents. Tranvik et al. (2009) summarize the importance of lakes as being: recipients of terrestrial organic carbon; reactors where primary production, mineralization, greenhouse gases, sedimentation, and carbon burial occur; and a reservoir of carbon dioxide. Therefore standing water bodies are a potential hot spot for DOC dynamics. Reservoirs are man-made water impoundments built for the purposes of drinking water supply, irrigation, hydropower generation and flood control. They can also serve as recreational facilities for fishing, bathing and water sports; however the reservoirs used in this study are strictly used only for drinking water purposes.

Lakes and reservoirs exhibit a dynamic heterogeneous characteristic which creates temperature and redox boundaries in the water and sediment. Shifts in redox conditions and temperature boundary influence biogeochemical processes at the sediment water interface hence making the sediment water interface a potential hot spot for mobilization and immobilization of various solutes. This thesis chronicles DOC exchange at the sediment water interface in standing water bodies by both focusing on fluxes, and understanding processes and drivers. In order to introduce these aspects, the following sections of the introduction are divided into the main themes of this thesis which are: methodological aspects of benthic flux determination, benthic DOC fluxes (processes and drivers), sediment resuspension effects and DOC quality aspects.

1.2 Methodological aspects of benthic flux determination

Solute fluxes at the sediment water interface can be quantified by various methods; benthic chambers, porewater concentration diffusion, *ex situ* sediment incubations, diffusion gradient in thin films gels (DGT) and changes in hypolimnetic concentration. Benthic chambers are regarded as most accurate for *in situ* fluxes measurements (Viollier et al. 2003); however, their application is laborious and requires sophisticated lander systems if they are to be used in deep areas. Diffusive fluxes from porewater gradients using diffusion based models can also be used (Berg et al. 1998); however, this method does not include advection and bioturbation. Moreover it requires concentration gradients with a sufficiently high spatial resolution which is more challenging to measure for DOC. The DGT method is also a promising technique

(Bondarenko et al. 2011) but it is fairly new and to my knowledge it has not yet been used for DOC. Changes in hypolimnetic concentration are laborious and require a high resolution depth concentration monitoring of the reservoir. For this reason they are not commonly used, although it can circumvent the problem of spatial heterogeneity of the sediment surface.

Ex situ sediment incubations are considered a more practical solution (Hammond et al. 2004). They can be run in a flow through mode with an inflow and outflow however this requires measurable concentration differences in the inflow and outflow. Very low fluxes can be difficult to measure since concentration differences might fall below detection limits. Flow-through systems also involve pumping water which in most cases has to be filtered to prevent clogging of tubes. In addition, depending on the flow rate biofilms can build up in the tubes and this can influence concentrations of certain solutes. To circumvent some of these problems closed batch core incubation can be used.

I wanted to quantify the seasonal progression of fluxes for a full year in three drinking water reservoirs and to address within reservoir heterogeneity by investigating riverine and lacustrine zones of the reservoirs. Therefore a method that would be manageable yet plausible for such an intensive initial investigation was required. I settled for an *ex situ* batch core incubation method which was modified to meet objectives of this study. The method was designed to mimic *in situ* conditions which imply that temperature and redox conditions control were critical aspects. In addition the incubation had to be short enough to circumvent problems associated with long term incubations. For example an *ex situ* closed batch core incubation in the long run cannot account for differences due to sedimentation of fresh particles, which happens *in situ*. Groundwater interactions are also excluded; however, they might be irrelevant in the reservoirs investigated, considering the bedrock type (Halbedel and Koschorreck 2013). Another aspect relates to the dependency of diffusion process on the concentration gradient which implies that long term incubation will result in equilibration of the porewater concentration and overlying water concentration especially in a set up with lower volume of overlying water. I also focused on initially measuring fast fluxes like oxygen and then later determination of the slower fluxes.

The method was developed taking into consideration all aspects and issues raised above. Through this method it was possible to measure the benthic fluxes of DOC and other solutes, which I introduce in the next section.

1.3 Benthic DOC flux: processes and drivers

In standing water bodies DOC is either imported from the catchment or produced/mobilized through internal processes. The internal mobilization/production processes include algal production (Jonsson et al. 2001), diffusion from sediment porewater with high solutes concentrations (Burdige et al. 1992; Sachse et al. 2001), sediment resuspension (Koschinsky et al. 2001), and mineralization of sedimenting detritus (Wetzel 1995; Wetz et al. 2008). The mechanisms behind the mobilization and immobilization of DOC are both biotic and abiotic and lead to formation and degradation of particulate organic matter (POM). For each of internal mobilization/production process there is a counter immobilization/consumption process.

The major immobilization/consumption processes are: 1) adsorption and desorption from mineral surfaces (Kaiser et al. 2001; Koelmans and Prevo 2003), 2) mineralization of POM and consumption of DOC by heterotrophic bacteria (Wetzel 1995; Le Moigne et al. 2013), 3) aggregation/coagulation of DOC and dissolution of the DOC colloids (Komada and Reimers 2001; Von Wachenfeldt and Tranvik 2008). The net concentration of DOC in a standing water body therefore depends on the difference between magnitude of mobilization and immobilization of DOC. Many studies have addressed DOC turnover in standing freshwater bodies (Wetzel 1992; Sondergaard et al. 2000; Bastviken et al. 2004; Guillemette and Del Giorgio 2012) however to the best of my knowledge little is known about benthic DOC exchange. Processes leading to benthic DOC exchange are summarized in a conceptual model in Fig. 1.1.

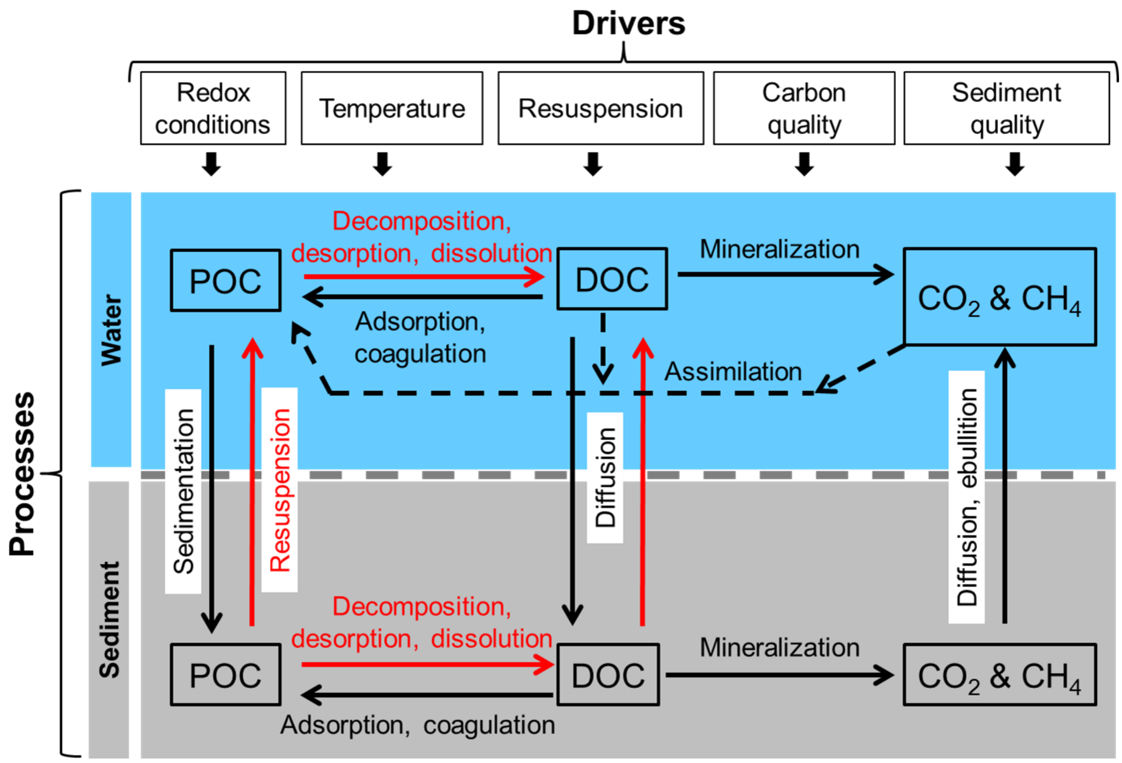


Fig.1.1. Benthic DOC mobilization (red arrows) and immobilization (black arrows) processes, and drivers influencing DOC exchange.

Benthic DOC mobilization and immobilization processes are driven by a number of factors; the main factors have been summarized in Fig.1.1. In the following section I dwell on how the driving factors (drivers thereafter) can influence the processes I have already mentioned. The focus will be on individual drivers however due to the complexity of the influences they cannot be entirely separated hence reference to all associated drivers will be made in each particular paragraph.

Redox conditions/potential refers to the tendency of chemical species to acquire electrons leading to a reduced state. The sequential reduction of oxygen, nitrate, manganese, iron, sulphate and carbon dioxide occurs in aquatic systems. Depletion of oxygen results in a state of anoxia. Under anoxic condition solutes exist in their reduced state but when exposed to oxygen they will be oxidised. This redox shift is important when considering the adsorption of DOC and phosphorus (P) to oxidised iron oxyhydroxides (Einsele 1936; Mortimer 1942; Tipping 1981; Davis 1982; Knorr 2013; Sodano et al. 2016). On reaching the oxic zone iron will be oxidised from Fe(II) to Fe(III) and then hydrolysed to oxyhydroxides (Stumm and Morgen 1996), which will adsorb DOC and P. This immobilization process has been demonstrated in many other studies (Mc Dowell 1985; Guggenberger et al. 1998; Kalbitz et al. 2000; Skoog and Arias-Esquivel 2009; Chen et al. 2014). It is therefore expected that under oxic conditions, in the overlying water, the release of DOC from anoxic DOC rich sediments is impeded by this process. Reducing conditions also preserve organic matter (OM) because certain enzymes require molecular oxygen (Fenner and Freeman 2013). Redox conditions also play an important role in mobilization and immobilization of other solutes e.g. the coupling of the Fe and sulphur cycle. Anoxic conditions leads to sulphate reduction and formation of hydrogen sulphide, which in turn reacts with ferrous iron to from iron sulphides (Roden and Edmonds 1997; Blodau and Peiffer 2003; Koschorreck et al. 2007). This immobilization of Fe will lead to mobilization of DOC and phosphorus.

Temperature influences microbial processes, which are responsible for benthic DOC turnover. Temperature effects on benthic DOC exchange are both direct and indirect. The direct effect pertains to mineralization/degradation of POM, which in turn result in production of DOC. The direct effect of temperature therefore leads to consumption of oxygen and this can lead to anoxia, depending on the rates of the mineralization. Anoxia in turn as mentioned earlier on will lead to reductive dissolution of Fe minerals leading to desorption of DOC from Fe. This elevates porewater DOC concentration to levels higher than what is in the overlying water (Boto et al. 1989; Burdige et al. 1992; Alperin et al. 1999; Sachse et al. 2001). The concentration gradient will favour diffusion of DOC from porewater into the overlying water until equilibrium is reached. Therefore both direct and indirect temperature effects are expected to mobilize DOC. However the fate of this DOC depends on redox conditions in the water column, which is explained in the next paragraph.

Sediments are generally anoxic with only up to a few mm being oxic in some cases (Rasmussen and Jorgensen 1992). Porewater contains elevated concentration, which can be due to reduced consumption under anoxic conditions. Mclatchey and Reddy (1998) found out that organic matter mineralization in soils decreases with decreasing redox potential and Bastviken et al. (2004) observed a more extensive organic matter mineralization under oxic and anoxic/oxic conditions than under anoxic conditions. As the DOC diffuses into the oxic zone of the sediment/overlying water there are changes with regards to solute redox states and microbial metabolism. Burdige and Homstead (1994) found out that there is enhanced biological consumption of DOC in the uppermost sediment. The oxic zone can be deeper than usual due to bioturbation and this promotes redox oscillations which can lead to rapid mineralization of benthic organic matter (Aller 1994). Therefore, DOC diffusing out of the porewater might not reach the overlying water; however, this might depend on the thickness of the oxygen diffusive boundary layer (DBL). The oxygen DBL is temperature sensitive.

From the temperature dependency of microbial mineralization/degradation seasonal differences in porewater DOC production and consumption are expected. Seasonal differences can also be due to the quantity and quality of the organic matter. Most of the organic carbon that accumulates in sediment in winter is not fully mineralized because of lower temperatures (Den Heyer and Kalff 1998; Gudasz et al. 2015). It is therefore expected that as temperature increase in spring/early summer there is an increased mineralization of organic matter and subsequent increase in DOC concentration.

The redox dependent relationship between Fe and DOC is important for mobilization/immobilization of both solutes. Dissolved organic matter and Fe interaction have been extensively studied in soils unfortunately there is still a dearth of knowledge about these interaction in freshwater sediments. The interaction of Fe and DOC can occur through many mechanisms; 1) anion exchange, 2) ligand exchange surface complexation, 3) hydrophobic interaction, 4) entropic effects, 5) hydrogen bonding and 6) cation bridging (Baham and Sposito 1994; Kahle et al. 2004). The ligand exchange is between DOC and Fe hydroxyl groups on mineral surfaces (Shen 1999; Saidy et al. 2013). Mineral surface sorption capacity of DOC in soils has been found to be related to clay content (Shen 1999; Kaiser and Zech 2000; Saidy et al. 2013), ionic strength and pH (Shen 1999; Chen et al. 2014). Presence of salt enhances adsorption via electrostatic interactions. The adsorption depends also on DOC quality. DOC fractions with high molecular weight, higher molar adsorptivity, lower acidity and lower hydrophilicity are preferentially adsorbed by soil minerals (Maurice et al. 2002; Guo and Chorover 2003). Iron adsorbs also other negatively charged solutes, hence potential competition for adsorption among solutes. Grafe et al. (2001) found DOC to be the preferred sorption partner for ferrihydrite and goethite and Zak et al.

(2004) found out that DOC was preferentially retained ahead of phosphorus. However Hunt et al. (2007) demonstrated that phosphorus inhibits DOC adsorption to Fe. It is also important to consider the reversibility of the DOC/Fe mechanism because of the potential implications on availability of both Fe and DOC. Guo and Chorover (2003) found out that adsorbed DOC was not completely desorbed when placed in DOC free water. The Fe and DOC interactions are therefore complex since many factors are at play.

The adsorption of DOC to Fe minerals depends on the availability of Fe as a sorption partner. Most freshwater systems are Fe rich in comparison to marine systems, however, in sulfidic sediments sulphate reduction may result in the immobilization of Fe through formation of iron sulphides (Roden and Edmonds 1997; Taillefert et al. 2002; Van Der Welle et al. 2006). If that happens then the amount of reduced Fe reaching the oxic zone of the sediments during the diffusion process will be low. This implies reduced sorption partners for DOC and P which can lead to accumulation of DOC and P in the overlying water despite the water being oxic.

Redox conditions and temperature in the aquatic ecosystem are seasonal; therefore my experiments were designed to follow the seasonal dynamics of the two drivers. Anoxia occurs in the overlying water of lakes with summer stratification. Two of the investigated reservoirs are deep and have summer stratification. I was therefore interested to determine the role of anoxia on benthic solute fluxes. The duration and extent of anoxia in terms of surface area was also of interest for determining solutes budgets. For this reason two sampling points were selected in these reservoirs: one which was shallow and oxic all the time; and another which was deep and with anoxia from summer until autumn reservoir mixing.

In the previous paragraphs I elaborated the influence of redox conditions and temperature on DOC mobilization/immobilization, and the complex potential interaction of the two drivers. Both processes are affected by carbon quality and also sediment quality. Sediment quality also includes carbon quality but for purposes of clarity it is used here to refer to mineralogical properties of sediments. The role of carbon quality is explained in a separate section below. Different sediment minerals have different surface areas and this will influence the quantity of bacteria that can be harboured by the sediment surface. Jiang et al. (2007) found out that adsorption of the heterotrophic bacteria *Pseudomonas putida* to mineral surfaces was in the order goethite > kaolinite > montmorillonite. Grain size distribution of the sediment will also influence other factors e.g. oxygen penetration depth. Oxygen will penetrate deeper in coarser sediments compared to finer sediments. The role of sediment mineralogy is important however I do not go into detail in this thesis. I focus on general sediment characterization i.e. loss on ignition, water content to explain differences that might be related to sediment mineralogy. The next section looks at the role of DOC quality as a driver of benthic DOC mobilization/immobilization.

1.4 DOC quality

In a bid to understand the rising trend of DOC in surface waters, a lot of work has been done to quantify DOC from different compartments of the ecosystem. This is a crucial component for the holistic understanding of the DOC problem. We learnt in the previous section that effects of redox conditions and temperature will also depend on the DOC quality; hence inclusion of DOC quality further enhances understanding of benthic DOC mobilization/immobilization. Unfortunately, research on DOC quality has been lagging behind due to lack of analytical methods, and complexity of DOC compounds, which require advanced methods to isolate (Woods et al. 2011; Sillanpää et al. 2015). Over the years many methods to characterise DOC have been developed: 1) bulk parameters (total organic carbon -TOC, DOC, specific ultraviolet absorption – SUVA); 2) spectroscopic methods (fluorescence, ultraviolet and visible absorption spectroscopy - UV-vis, fourier transform infrared spectroscopy - FTIR, nuclear magnetic resonance - NMR); 3) chromatographic methods (high pressure size exclusion chromatography - HP-SEC, flow field flow fractionation - FIFFF); and 4) mass spectrometric methods (liquid chromatography mass spectrometry - LC-MS, fourier transform ion cyclotron resonance mass spectrometry - FTICR-MS, gas chromatography mass spectrometry - GC-MS). All these methods have different pros and cons, which are summarized well by Matilainen et al. (2011). With the advent of FTICR-MS method, inroads are being made in unravelling the complex DOC compounds. However there are still challenges of data interpretation emanating from complexity of organic carbon compounds (Matilainen et al. 2011).

DOC quality is important because it helps in understanding the extent to which a compound has been degraded, predict likelihood of further degradation and potential degradation pathways. All this information helps to understand how DOC compounds will persist in the environment and the potential pathways of immobilization. For example DOC is known to be selectively adsorbed to iron minerals depending on its quality (Maurice et al. 2002; Kothawala et al. 2012a). This information is not only important for lakes and reservoirs water quality management, but also for drinking water treatment plants. For drinking water suppliers such information is important in finding efficient DOC removal methods.

In this work both bulk parameters and FTICR-MS were combined to understand overlying water and benthic DOC dynamics in drinking water reservoirs pre-dams. Dissolved organic carbon quality and quantity differences between the surface, hypolimnetic and porewater of riverine and lacustrine zones were determined. Riverine zones are characterised by a high input of allochthonous DOC and are therefore expected to contain more aromatic lignin derived DOC (Lind 2002). Lacustrine zones are characterised by more autochthonous less aromatic algae derived DOC (Lind 2002). Furthermore surface water and bottom water in riverine zones is expected to be of similar quality and quantity because of the complete mixing. On the other hand a gradient in both DOC quantity and quality is expected between lacustrine zone surface and bottom waters, due to their stratified nature between spring and autumn. Lacustrine surface water is expected to have oxic, higher temperature water while the bottom water is most likely to be anoxic (or to have lower redox potential) and lower in temperature. In the next section, which focuses on sediment resuspension, we again see the potential effects of DOC quality.

1.5 Sediment resuspension

Sediment resuspension is usually seen as a detrimental process in aquatic systems because it releases nutrients (Reddy et al. 1996; De Vicente et al. 2010), increases turbidity and reduces light penetration (Scheffer et al. 2003). Most literature on sediment resuspension has focused on nutrients (nitrogen and phosphorus). Not much is known about the effects of resuspension on benthic DOC exchange. This study therefore focused on DOC, nutrients and metals. Sediment resuspension is triggered by wind (Bloesch 1995; Tammeorg et al. 2013; Liang et al. 2016), and feeding activity of benthivorous fish (Søndergaard et al. 1990; Zambrano et al. 2001; Persson and Svensson 2006; Fischer et al. 2013). Resuspension mainly occur in shallow aquatic systems (Ogilvie and Mitchell 1998; Liang et al. 2016) however resuspension in deep systems also happens (Bloesch 1995; Tammeorg et al. 2013).

The concentration of DOC in pore water is usually higher than overlying water. Therefore, sediment resuspension is expected to increase the overlying water DOC concentration. The sediment is also a source of heterotrophic bacteria which implies that resuspension will introduce more bacteria quantity and diversity into the water. This can increase DOC degradation because: 1) benthic bacteria will be exposed to overlying water DOC, which might be of a better quality (less recalcitrant and aromatic) than benthic DOC; 2) particle adsorbed DOC will become available to overlying water bacteria enabling degradation; and 3) change in redox conditions from anoxic in the sediment to oxic in the overlying water can lead to better degradation of DOC. Heterotrophic bacteria utilise DOC as an energy source leading to decrease in DOC concentration, however this process also depends on the DOC quality. Microorganisms will utilize the easily degradable substances first. Recalcitrant DOC might take extremely long to be degraded and will therefore remain in the system for a long time. The DOC quality will also determine whether it is easily adsorbed to mineral surfaces and thereby immobilized. Change in redox conditions can also have a negative short term effect to the activity of bacteria as they have to adjust to the resuspension disturbance and this can result in decreased degradation potential.

1.6 Objectives

Earlier sections of the introduction chronicled the DOC problem and the social, health, and ecological concerns arising therefrom. They also detailed the importance of lakes and reservoirs as biological reactors in a catchment, and the relevance of the sediment water interface to quantify solute exchange and for understanding processes. I gave an overview of the benthic flux methods and why a batch sediment incubation method was selected, including critical aspects the methods had to address. I also presented a conceptual model (Fig. 1.1.) highlighting sedimentation, resuspension, diffusion, mineralization, adsorption as the main processes in DOC mobilization/ immobilization; which are driven mainly by redox conditions, temperature, resuspension, carbon quality, and sediment quality. This thesis primarily focused on investigating the aforementioned processes and drivers and how they influence benthic DOC fluxes in three drinking water reservoir pre-dams. This was achieved by using batch core sediment incubation, microbiological (Biolog EcoPlates) and DOC quality (FTICR-MS) methods and incorporating a multi-parameter approach. The objectives of the study were:

i. Development of a method to measure DOC flux between the sediment and water.

ii. Quantification of magnitude and direction, and identification of the major drivers regulating benthic DOC flux.

iii. Determination of how resuspension events affect direction and magnitude of DOC flux and other solutes at the sediment water interface.

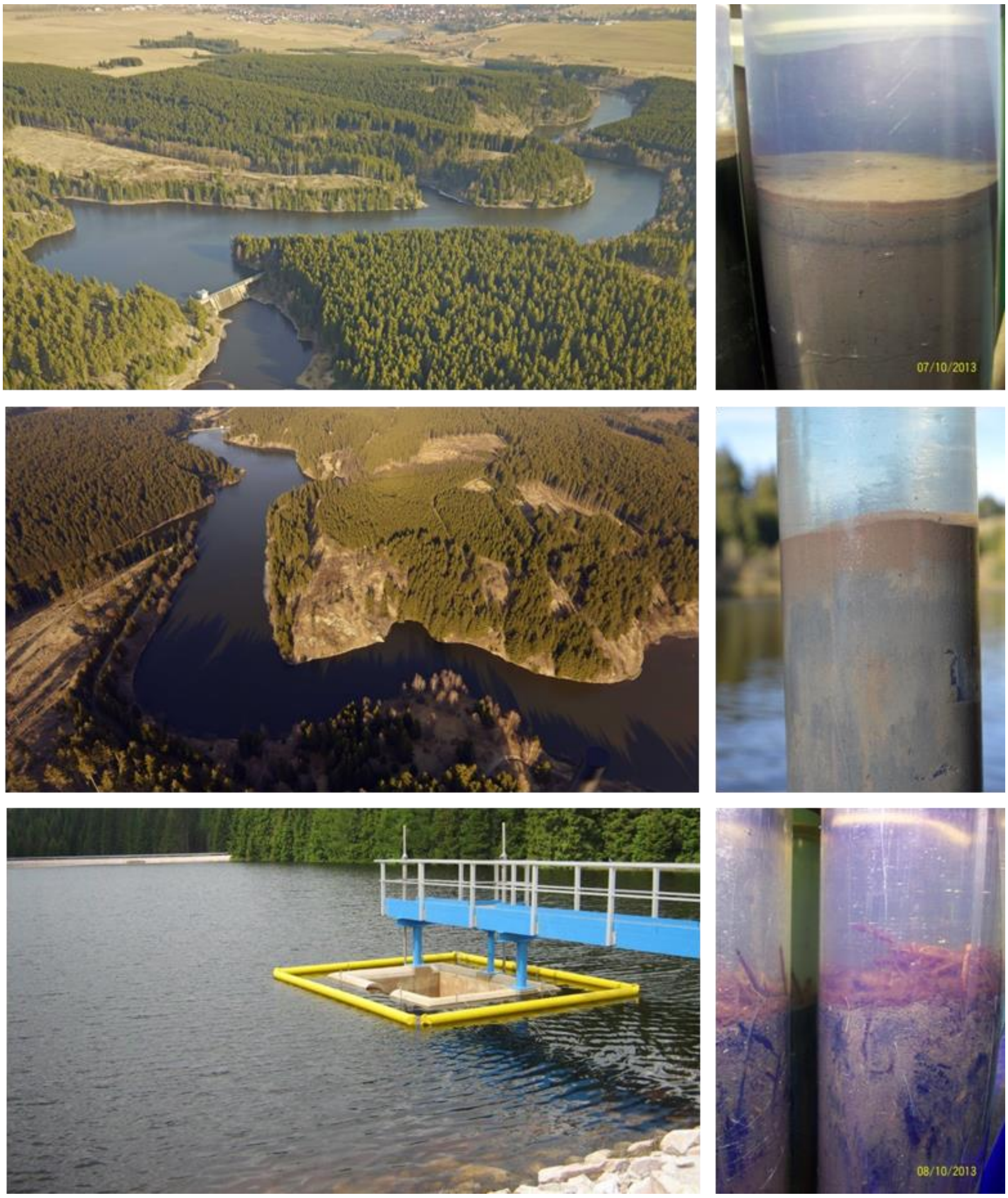
iv. Identification of potential mechanism(s) behind benthic DOC flux regulation.

v. Analysis of DOC molecular composition in water and porewater, and in sediment incubation overlying water exposed to different redox conditions.

1.7 Thesis structure

The following sections of the thesis are arranged as follows. Chapter 2 gives an overview of the study sites and methods employed in the study. Chapter 3 details the sediment incubation method, which is the main method used in this thesis. Chapter 4a looks at benthic DOC fluxes in the Hassel pre-dam. Chapter 4b looks at the benthic DOC fluxes in all the pre-dams studied and draws comparison and differences between the systems. Chapter 5 explores the role of sediment resuspension on DOC fluxes. Chapter 6 focus on DOC quality. Chapter 7 is a summary of the major results and discussion thereof and also highlights implications on lakes and reservoir management.

Chapter 2: Study sites and methods



Photos: Hassel (top), Rappbode (middle), and Rote Mulde (bottom) pre-dams (left panel) and the corresponding sediments (left panel). Pre-dam photos by A. Künzelmann, Helmholtz Centre for Environmental Research – UFZ; sediment photos by Tallent Dadi

2.1 Overview

In this chapter I summarize characteristics of the 3 pre-dams (Hassel, Rappbode, and Rote Mulde). I also give an overview of the methods used, calculations made, and statistical analysis employed. For more detailed information please refer to the publications and manuscript in the following chapters.

2.2 Study sites

This work was carried out in the Rappbode and Muldenberg reservoirs systems, in particular, in the Hassel and Rappbode pre-dam (Rappbode reservoir system) and Rote Mulde (Muldenberg reservoir system), all located in Germany (Fig. 2.1). In Germany, many drinking water reservoirs have a smaller reservoir upstream for each river channel feeding into the main reservoir. The smaller reservoirs herein referred to as pre-dams serve as sedimentation basins to reduce loads of suspended particles and dissolved nutrients, especially phosphorus, into the main reservoirs (Pütz and Benndorf 1998; Paul 2003). The principle behind nutrient load reduction is that high nutrients concentration water is retained in the pre-dams for some days which allow growth of phytoplankton hence utilisation of nutrients (Benndorf and Pütz 1987a; Benndorf and Pütz 1987b). The detritus will then sediment into the sediment of the pre-dam. Through this biological mechanism water flowing out of the pre-dam has a comparatively lower nutrient concentration than water flowing into the pre-dam from the catchment. Pre-dams functions as biological reactors and are a hot spot for various biogeochemical processes hence they are more interesting for catchment reservoir interaction studies.

Hassel, Rappbode and Rote Mulde pre-dams were also selected because: 1) they are drinking water reservoir pre-dams, and 2) they have exhibited the trend of increasing DOC concentration (Tittel et al. 2013) over the last years with the Rote Mulde falling in the region with a significant increase in DOC concentration (Sucker et al. 2011). Hassel and Rappbode have very similar morphometry, hydrological and water quality properties however Hassel is eutrophic and Rappbode is mesotrophic. Rote Mulde is relatively smaller than the other two, has a higher DOC concentration and a lower pH (Table 2.1). The pre-dams have also been described in previous studies (Rinke et al. 2013; Friese et al. 2014; Wendt-Potthoff et al. 2014).

Table 2.1: Pre-dam morphometry, hydrological and water quality properties and sampling periods. Data collated from various sources: Rinke et al. (2013), Tittel et al. (2013), Friese et al. (2014), and Wendt-Potthoff et al. (2014)

Pre-dam	**Hassel**	**Rappbode**	**Rote Mulde**
Volume [1000 m^3]	1448	1146	62
Surface area [km^2]	0.288	0.218	0.098
Max. depth [m]	14	17	3.5
Mean depth [m]	5.0	5.7	0.6
Residence time [d]	65	52	6
Discharge [m^3 s^{-1}]	0.65	0.73	0.12
Catchment area [km^2]	44.6	47.6	5.4
Catchment land use;			
Forest	37%	72%	98%
Grasslands	33%	22%	1%
Agriculture	25%	2%	0%
Other	5%	3%	1%
pH	6.5 - 9.6	6.5 - 8.4	5.0 - 6.9
Conductivity [mS cm^{-1}]	0.26	0.19	0.08
Sampling sites	Shallow (3.5 m), Deep (13 m)	Shallow (4 m), Deep (16 m)	Shallow (3.5 m)

Hassel and Rappbode stratify in summer due to their morphometry, while Rote Mulde is completely mixed. The summer stratification in Hassel and Rappbode resulted in selection of two sampling points in these locations; a shallow point without stratification and a deep point with stratification. Rote Mulde pre-dam had been drained a few years prior to sampling to enable some construction work on the pre-dam. As a result vegetation started to grow on the exposed sediments. At the time of sampling the effects of the construction work were still apparent: real sediment layer was very thin (< 2 cm), and dead vegetation was still visible. The lower part of the sediment was from the period prior to construction and had been aggregated due to growth of vegetation. This made the sediment sampling challenging.

The geology and soil in the Hassel and Rappbode catchments consists of a siliceous parent material that is covered by nutrient poor cambisols and stagnic gleysols, with the gleysoils predominantly occurring in the valley bottoms, close to the riverbeds (Friese et al. 2014). Groundwater influenced gleysoils area is approximately twice in Hassel (about 10 km^2) than in the Rappbode catchment (Friese et al. 2014). The geology and soil in Rote Mulde consists of quartz-porphyry bedrock that is predominantly covered by peaty topsoil (Tittel et al. 2013). There is groundwater influence in the catchment streams, resulting in mobilization of DOC from groundwater (Tittel et al. 2013; Musolff et al. 2015). However groundwater influence might not be relevant to the pre-dams considering the bedrock type (Halbedel and Koschorreck 2013).

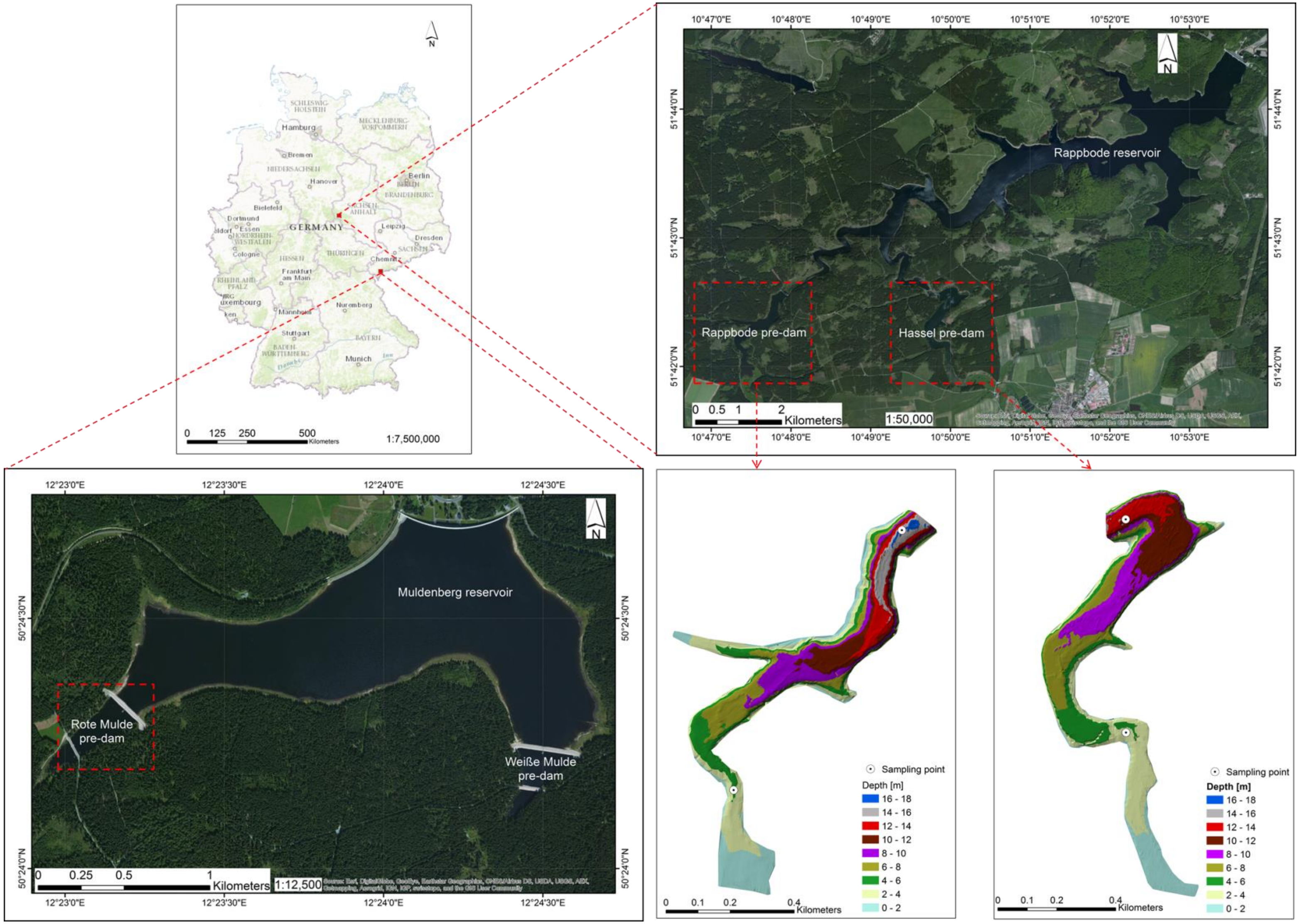


Fig. 2.1. Location of Rappbode (top right) and Muldenberg (bottom left) reservoir systems in Germany (top left), imagery maps of the systems showing the study sites: Hassel, Rappbode, and Rote Mulde pre-dams (red circles), and bathymetry maps of Hassel and Rappbode pre-dams.

2.3 Sediment sampling and incubation

Hassel and Rappbode were sampled 6 times a year to capture the main relevant times from snowmelt to just before autumn mixing. Rote Mulde was sampled 3 times a year: snow melt, summer, and autumn, for 2 consecutive years. For each sampling 4 replicate undisturbed sediment cores were collected in 60 cm long and 9 cm diameter core tubes. The cores were closed with special covers with stirring device to mix the overlying water (see Chapter 3). Sediment cores were transported back to the laboratory in insulated boxes. The hypolimnion water from each point was collected. This water was used for refilling the cores after sampling, and also for preparation of controls for the experiment. The controls were prepared by incubating the hypolimnetic water in glass bottles. This was done to distinguish sediments effects from changes occurring in the water. The sediment and control bottles were incubated in temperature controlled climate rooms at *in situ* conditions; (temperature and redox conditions). Incubations were carried out for 14 days and sampling of the overlying water and control was done once every 3 days.

Initially the oxygen consumption of all cores was measured with optical oxygen sensors (Pyro Science, Germany). A 30 ml water samples was sampled from each core and control bottles. The sampled volume was replaced with hypolimnion water at *in situ* oxygen and temperature conditions. Samples were analysed for DOC, $UV_{254\ nm}$, TIC, CH_4, NH_4^+, NO_3^-, soluble reactive phosphorus (SRP), SO_4^{2-}, Fe, and Mn. Dissolved organic carbon samples (12 ml) were analysed using a total organic carbon analyser (DIMATOC 2000; Dimatec Analysentechnik GmbH, Germany) after GFF filtration (DIN_EN_1484:1997-08 1997; Herzsprung et al. 1998). Ultraviolet absorbance at 254 nm samples (1 ml) were filtered using a GFF filter and analysed photometrically (DIN_38404-3:2005-07 2005) in a quartz cuvette (Hach Lange DR

500; Hach Lange, Germany). Total inorganic carbon and CH_4 samples (1 ml) were analysed using a gas chromatograph (SRI, USA). Ammonium was analysed using an ammonium ion-selective electrode with a separate lithium acetate reference electrode (ELIT 8051 and ELIT 003n; Nico2000 Ltd., UK). Nitrate and SO_4^{2-} (1.5 ml) were analysed by ion chromatography (DIONEX ICS-3000;DIONEX, Germany), based on the standard method (DIN_EN_ISO_10304-1 2009). Iron and manganese (1.5 ml) were analysed using an inductively coupled plasma mass spectrometer (Agilent 7500c ICP-MS; Agilent, Germany), based on the standard method (DIN_EN_ISO_11885:2009-09 2009; Baborowski et al. 2012). Soluble reactive phosphorus (SRP) samples (1 ml) were analysed photometrically (Cary 60 UV/Vis spectrophotometer; Agilent, Malaysia) based on the method of (Laskov et al. 2007).

A sample of 30 ml is relatively small for the parameters measured so all methods were adapted to a smaller sample volume. This was done to keep the sample volume replacement as low as possible compared to the overlying water volume in the cores, which was on average 1.4 litres. Therefore the sampled water volume was 2% of the overlying water volume. In addition pH, temperature and oxygen concentration were monitored during the incubation. Both air and water temperature was monitored in the climate room. For detailed explanation on sample preparation for each method please refer to Chapter 4a.

2.4 Sediment resuspension and sectioning

At the end of the incubation approximately 1 cm upper sediment layer in each core was manually resuspended using a glass rod. The cores were allowed to stand for 24 hours before the overlying water was sampled and analysed as above. The sediments were then sectioned into 0-1, 1-3, 3-5 cm layers. Part of the sediment was used for dry weight, water content and loss on ignition analysis. The other part was used for pore water extraction, which was done by centrifugation and analysed as above with the exception of NH_4^+ which could not be analysed because of inadequate sample volume. The minimum required volume for NH_4^+ was 5 ml.

2.5 Benthic microbial metabolic potential

The experiments were carried out to determine if there were differences in organic substrate utilisation before and after resuspension. This was done by using Biolog EcoPlates™ (Biolog, Inc., Hayward, California), which contain 31 common organic substrates and Azo dye, which is released upon utilisation of the substrate. When the plates are inoculated with a water sample the utilisation of the substrates can be monitored by measuring the absorbance (colour intensity) of each well over time. The before resuspension experiments water samples were taken from the pre-dams, at each site, just above the sediments. The after resuspension experiments water samples were taken from all the four resuspended cores and combined into one sample. Biolog EcoPlates were incubated at *in situ* temperature conditions and redox conditions. The plates were measured over time until the change in absorbance values became constant. Please refer to Chapter 5 method section for the detailed procedure.

2.6 Carbon budgets and burial rates

Carbon budgets were computed by quantifying the sediment area of the pre-dam overlain by anoxic and oxic water. This was done using biweekly measured pre-dam temperature and oxygen profiles (field data) and bathymetric data (echo sounding method). The thermoclines and oxyclines were determined from temperature and oxygen profiles data using the Lake Analyzer Version 3.3 software (Read et al. 2011). To determine the oxic DOC release, the DOC temperature dependency equation (derived from the sediment incubations) was applied to pre-dam biweekly temperature profiles, to get the DOC flux. The DOC flux was then multiplied by biweekly pre-dam oxic area. The anoxic DOC release was calculated by computing the product of the mean DOC flux for the anoxic period (obtained from the sediment incubations) and the biweekly pre-dam anoxic area from the oxygen profile data. The biweekly oxic and anoxic carbon release/uptake for the entire year were summed to give the annual sediment carbon budget. Similarly, total release of CH_4 and TIC was calculated. The sum of DOC, TIC, and CH_4 release is the total out flux of carbon at the sediment water interface.

To determine carbon sedimentation, sediment traps were deployed at 2 m in all shallow sites (Hassel, Rappbode, and Rote Mulde), at 6 m in all deep sites (Hassel and Rappbode), and at 12 m (Hassel deep site) and 14 m (Rappbode deep site). Sediment traps were deployed for periods ranging between 1 and 2 months, due to the low sedimentation rates in the pre-dams. Refer to Chapter 4a for detailed processing and analysis of material the from sediment traps. Carbon sedimentation was calculated by summing the product of the sedimentation rate at the shallow and deep sites, and the total shallow and deep surface areas. Carbon burial rates were computed as the difference between the carbon sedimentation and the total carbon out flux (sum of DOC, TIC, and CH_4), divided by the carbon sedimentation, and expressed as a percentage.

2.7 Hypolimnetic inventory

Hypolimnetic inventory is a benthic flux determination method that can be used in stratified lakes and reservoirs to determine the change in hypolimnetic concentrations of solutes during the stratified period. This was done by collecting bi-weekly data from the deep points of the Hassel and Rappbode for a full year, and at the shallow sites including Rote Mulde, only on the dates of sediment sampling campaigns. The data at deep sites was collected for determining *in situ* conditions for sediment incubation experiments, hypolimnetic inventories (only deep site), and as supporting water chemistry data. The data includes oxygen, temperature profiles, which were measured by multi-parameter probes (Idronaut, Italy; Sea & Sun Technologies, Germany), and a collection of water samples at depth: 0, 2, 5, 8, 10, 12 and 13/16 m (Hassel/Rappbode) at the deep site; and surface (0 m) and bottom (Hassel-3.5m, Rappbode-3.8 m, and Rote Mulde-3.5 m) water samples at the shallow sites. The samples were analysed for DOC and other parameters mentioned above in section 2.3. This data was used to calculate the hypolimnetic inventories based on the method of Wendt-Potthoff et al. (2014), highlighted in the equation below. The method was also used to calculate specific turnover rates for given periods coinciding with the dates of sediment incubation campaigns.

$$Turnover\ rate\ [mmol\ m^{-2}\ d^{-1}] = \left\{ \frac{\left(\left(\frac{end\ hypolimnion\ content\ [mmol]}{Surface\ area\ [m^2]}\right) - \left(\frac{start\ hypolimnion\ content\ [mmol]}{Surface\ area\ [m^2]}\right)\right)}{Duration\ [d]} \right\}$$

2.8 DOC quality determination

2.8.1 Solid phase extraction (SPE)

Glass fibre filter filtered water samples (50 ml) were acidified with hydrochloric acid to pH 2.0, and processed through Agilent PPL solid-phase cartridges to desalt the extract for subsequent electrospray ionization. A SmartPrep automatic cartridge extractor (Horizon / USA) was used for processing SPE. The methanolic extracts were diluted to 5 ml and the extracts were frozen before further analysis.

2.8.2 FTICR mass spectra determination and evaluation

The FTICR mass spectra determination was carried out by the Analytical Biogeochemistry Research Unit at the Helmholtz Centre Munich, German Research Centre for Environmental Health. High resolution FTICR mass spectra were acquired after electrospray ionisation (ESI) in the negative ion mode with an APEX Qe FTICR-MS (Bruker, Bremen, Germany) equipped with a 12 Tesla superconducting magnet and an Apollo II micro electrospray source. The finally generated elemental formulas were validated by setting sensible chemical constraints (element counts: carbon (C) ≤ 100, oxygen (O) ≤ 80, nitrogen (N) ≤ 6, and sulphur (S) ≤ 3). Further details are described in Herzsprung et al. (2010).

2.8.3 Data analysis

Formula assignment was executed as described in Herzsprung et al. (2014). The reliable carbon, hydrogen, and oxygen (CHO) formulas (CHON, CHOS and CHONS were not reconsidered) were exported to a spread sheet. Altogether, 13 samples were evaluated for calculation of inter sample rankings as described in Herzsprung et al. (2012b) by searching for components of the total common presence data pool. The inter sample ranks were calculated for 13 samples, and for visualization in van Krevelen diagrams ranks were used.

2.8.4 Cluster analysis / FTICR-MS elemental formula data

Cluster analysis was performed with the software STATISTICA 12 from Statsoft based on the rank intensities of the FTICR-MS peaks from the investigated 13 samples. The ranks of the intensities were calculated for each sample as described in Herzsprung et al. (2012b). The Ward method with squared Euclidian distance was used because it is based on a classical sum-of-squares criterion, yielding groups that minimize within-group dispersion at each binary fusion (Murtagh and Legendre 2014).With a z-score scaling as data pre-treatment the expected value (average) of each series became 0 and the standard deviation 1.

2.9 Calculations and statistics

Solute fluxes were calculated from the changes in concentration over the incubation period divided by core surface area. Resuspension fluxes were calculated as the difference between concentrations prior and after resuspension divided by core surface area and the fluxes were expressed per event basis. All statistics were calculated using SPSS version 22 and are specified in the corresponding chapters.

Chapter 3: A sediment core incubation method to measure the flux of dissolved organic carbon between sediment and water

Tallent Dadi, Corinna Völkner, Matthias Koschorreck

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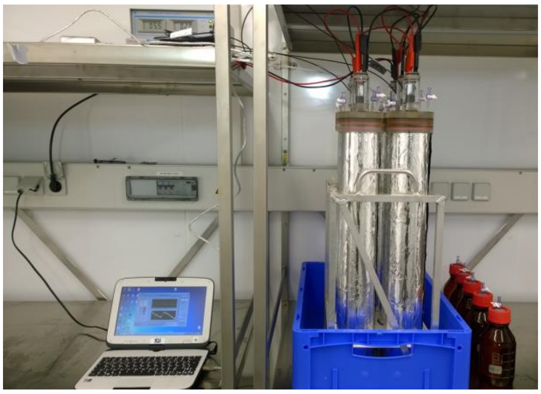

Photo: Sediment core incubation set up (controls are the bottles with red caps). Photo by Tallent Dadi

Overview

The publication describes methodological aspects of *ex situ* batch core sediment incubation method under controlled *in situ* conditions, for measurement of DOC and other solutes fluxes. It provides a detailed description of the sediment core cover design, which was the most critical part of the method. The method distinguishes fast fluxes e.g. oxygen and slow fluxes e.g. DOC. The former are initially measured within 24 hours followed by the measurement of the later within a 14 day incubation period. During the 14 day period slow fluxes are determined through repeated sampling and analysis. In addition to the successful determination of DOC through the method, the publication also reveals the unsuitability of using ultraviolet absorption at 254 nm ($UV_{254\ nm}$) as a DOC concentration proxy under anoxic conditions.

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IASWS 2014: THE INTERACTIONS BETWEEN SEDIMENTS AND WATER

A sediment core incubation method to measure the flux of dissolved organic carbon between sediment and water

Tallent Dadi[1] · **Corinna Völkner**[1] · **Matthias Koschorreck**[1]

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Abstract

Purpose The exchange of dissolved organic carbon (DOC) between sediment and water likely has an impact on aquatic DOC quantity and quality. Therefore, we developed a method to measure the flux of DOC between sediment and water.

Materials and methods We constructed Plexiglas sediment core covers, which enable the stirring of the overlying water, continuous measuring of the oxygen concentration, adding and/or withdrawal of water, bubbling and microsensor measurements at the sediment-water interface. Sediment cores from two pre-dams of drinking water reservoirs were incubated in a set-up allowing the measurement of benthic fluxes of DOC and other solutes, including oxygen, dissolved nutrients and metals.

Results and discussion Dissolved organic carbon fluxes were low and influenced by the redox conditions in the bottom water. We tested whether UV absorption (UV_{254}) can be used as a fast method to monitor DOC changes in the core incubations. There was a good correlation between UV_{254} and DOC only at shallow, oxic sites. In anoxic waters, UV_{254} was strongly influenced by iron. The fluxes of DOC and other solutes, especially oxygen, differed by more than 1 order of magnitude. Thus, a two-step incubation, measuring first the fast fluxes followed by a 14-day incubation, is recommended. Sulfate reduction appeared to be the most important process of organic matter mineralisation under anoxic conditions, while aerobic respiration and, to a lesser extent, denitrification dominated under oxic conditions.

Conclusions We present a set-up that allows measuring the flux of DOC as well as of other solutes between sediment and water. UV_{254} can be used as a proxy for DOC at oxic sites after establishing a site-specific calibration. Special care has to be taken to maintain redox conditions constant and to prevent oxygen depletion or contamination by atmospheric oxygen. The flux of DOC might be coupled to the reductive dissolution of iron minerals.

Keywords Benthic flux · Dissolved organic carbon · DOC · Sediment core incubation · UV_{254}

1 Introduction

The exchange of solutes between sediment and water is an important process in aquatic biogeochemical cycles and has a profound influence on water quality of surface waters. While the flux of oxygen, nutrients and redox-active compounds has been intensively studied, not much is known about the exchange of dissolved organic carbon (DOC) between sediment and water. To fully understand the aquatic carbon cycle, an understanding of benthic DOC fluxes, their direction and regulation is essential. Thus, a practical method to measure benthic fluxes of DOC is needed. The measurement of DOC fluxes poses some serious challenges, as explained in the following paragraphs.

Various methods to measure benthic solute fluxes are available. Benthic chambers probably provide the most accurate information about in situ fluxes (Viollier et al. 2003). However, their application is laborious and, without sophisticated lander systems, their use is restricted to shallow areas. Also, if fluxes are very low, long incubation times are required,

Responsible editor: Carolyn Oldham

✉ Matthias Koschorreck
matthias.koschorreck@ufz.de

[1] Department of Lake Research, UFZ - Helmholtz Centre for Environmental Research , Brückstr. 3a, 39114 Magdeburg, Germany

which are difficult to realise with benthic chambers. This is because the fluxes of different solutes have different magnitudes. Namely, the flux of oxygen is usually high while we expect low fluxes of DOC (Gale and Reddy 1994; Zheng et al. 2011). This may lead to complete oxygen depletion and redox change during DOC flux measurements which possibly has an impact on the DOC flux. Ideally, if low fluxes are to be measured, the concentrations of all faster diffusing solutes must be held constant, which is difficult to realise in benthic chambers.

Ex situ sediment core incubations provide a practical solution (Hammond et al. 2004). Running them in a flow-through mode ensures constant conditions above the sediment. This method, however, requires a measurable concentration difference between the inflow and outflow. Very low benthic fluxes result in concentration differences below the analytical detection limit. The only way to circumvent this problem is to run the incubation in a closed batch mode and to make sure that other relevant solutes, especially oxygen, are not depleted during the incubation (Sommer et al. 2008).

A principally different way to determine benthic fluxes is to calculate them from vertical concentration gradients, using diffusion-based models (Berg et al. 1998). This approach, however, is difficult to realise for DOC, since it is challenging to measure DOC gradients with sufficiently high spatial resolution. A possible solution might be the use of diffusion gradient gels (DGT) (Bondarenko et al. 2011), but to our knowledge, these have not yet been used to measure vertical DOC gradients in sediments.

In this paper, we describe a batch core incubation method to measure DOC fluxes between sediment and water. Since we expect the flux to be influenced by redox conditions, special care was taken to keep the redox conditions at the sediment surface as constant as possible. This is especially crucial if there is a long time lag, typically caused by transport time, between taking the core and starting the incubation in the laboratory.

Sediment core incubations should be as short as possible. This means that we must either know the necessary incubation time beforehand or need a fast method which gives us information about the actual state of the incubation. While the oxygen concentration in long-term incubations can easily be monitored using online sensors, for the quantification of DOC, samples have to be taken, filtered and analysed in a DOC analyser. A fast and simple method which provides information regarding the DOC concentration in the water above the sediment cores would be highly useful. The measurement of UV absorption at 254 nm (UV_{254}) might provide a possible solution. This method is widely used to monitor DOC concentrations in surface waters (Matilainen et al. 2011; Rinke et al. 2013). However, UV_{254} only measures an optically active fraction of the DOC and plots of UV_{254} versus DOC are typically scattered. Thus, we investigated whether UV_{254} can be used to measure benthic DOC fluxes with sufficient accuracy.

2 Materials and methods

2.1 Set-up

We constructed Plexiglas sediment core covers which enable stirring of overlying water, continuous measurements of the oxygen concentration, adding and/or withdrawal of water, bubbling and microsensor measurements at the sediment-water interface (Fig. 1). The basic design was adapted from the set-up of Jo Banks (Abell et al. 2011). The stirrer was driven by a magnetic coupler. Together with the use of three O-rings, this made it possible to keep the core gas and water tight. The motor (Igarashi, Japan) allows slow stirring rates (1.5 turns per s) which is essential to mix the water but not to re-suspend sediment. There is a 20-mm-diameter working opening which can be used to enter microsensors. This opening has a thread and is sealed by a Plexiglas screw with an O-ring. The same opening was also used to remove gas bubbles. A separate part containing a 9-V battery and a custom-made speed regulator could be plugged on top. The battery allows stirring the cores in the absence of an external power supply for up to 8 and 15 h at 2.3 and 1 turns per s, respectively.

2.2 Field procedure

Sediment samples were taken from two pre-dams of drinking water reservoirs in central Germany. Hassel pre-dam is located in the Harz Mountains (51.74° N, 10.89° E) (Rinke et al. 2013). It is stratified over the summer months and develops an anoxic hypolimnion (~4 m below water surface) between June and November. Hypolimnion temperatures never exceed 6 °C, while the temperature at 4 m in depth fluctuates seasonally between 4 and 18 °C. Hassel pre-dam was sampled bi-monthly between April and November 2013. This paper focuses on the November sampling, which was at the end of the stratified period. We sampled one site at 4 m in depth, where the sediment surface was oxic throughout the year, and another site at the deepest point of 12 m in depth, which had been anoxic from June to November 2013.

The shallow Rote Mulde pre-dam (50.40° N, 12.38° E) of the humic substance rich Muldenberg reservoir in the Ore Mountains (Wobus et al. 2003) has a maximum depth of 4 m and was always fully mixed and oxic.

Sediment cores (9 cm in diameter) were taken with a gravity corer (UWITEC, Mondsee, Austria). Very short cores were pushed up using water-soaked floral foam (Mosy GmbH, Thedinghausen, Germany) in order to reduce the water volume. The floral foam was soaked to saturation in a bucket of water, the core was lowered into the water, the grey rubber

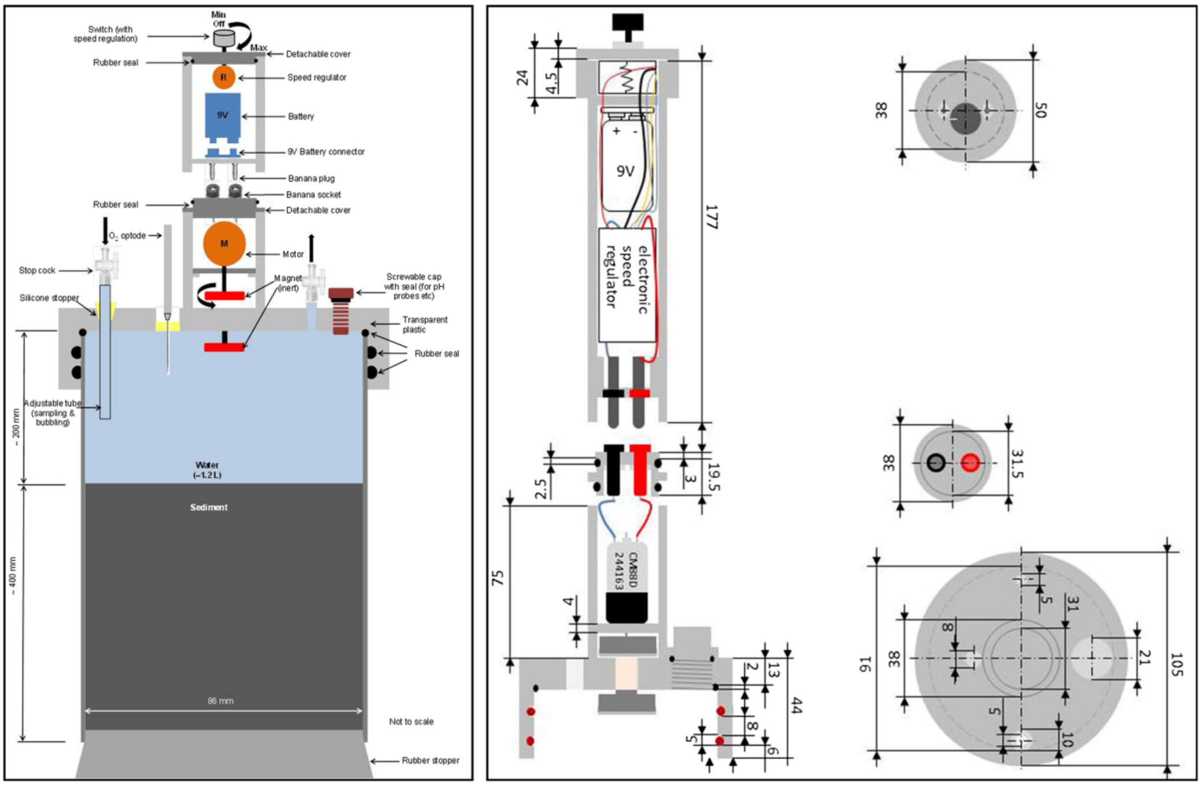

Fig. 1 Drawing of sediment core head (*left*) and technical drawing of the stirring core head (*right*)

stopper on the core was removed, and then the core was pushed onto the water-saturated foam, thereby incorporating the water-saturated foam into the bottom of the core. Finally, the grey stopper was inserted to close the bottom of the core. Bottom water for core filling and control incubations was taken about 0.5 m (after determination of the water depth) above the sediment using a standard 2-l water sampler (Hydrobios, Kiel, Germany) and filled in glass bottles. If the water sample contained visible suspended particles, it was discarded. The cores were immediately transferred into a custom-made Styrofoam transport box. This box was made of standard isofoam plates which were glued one above the other and in which then holes for the cores were drilled. Then, the standard lids of the cores were replaced by the stirring heads described above. The cores were filled up with bottom water through the microsensor working opening. Air bubbles were removed by gently tilting the cores and lateral hits. Then, the screw plug was screwed into the opening while excess air and water were allowed to leave through the opened Luer connectors, which were finally closed. When no gas bubbles were visible, the battery compartment was plugged in and stirring of the cores was started. The whole transport box with the stirred cores was then closed by an isofoam cover.

2.3 Laboratory procedure

Upon arrival in the laboratory, the cores were checked for gas bubbles which were eventually removed. Sediment cores were incubated at in situ temperatures in a climate chamber to an accuracy of ±1 °C. They were wrapped with aluminum foil to prevent light penetration. Each core was equipped with an optical oxygen (O_2) sensor (Pyro Science, Germany), and the battery compartment was replaced by an electric power supply from an adjustable transformer. The oxygen concentration in the cores was checked, and any oxygen was removed from the cores that were supposed to be anoxic. This was done by bubbling with a mixture of nitrogen and carbon dioxide (99.96 % N_2/0.04 % CO_2) until they were anoxic. Mixed nitrogen and carbon dioxide gas was used to maintain a constant pH level. The gas was bubbled through the port extending down to the sediment-water interface. Gas release was through the other port, which was equipped with a syringe without a plunger which was half filled with bottom water. This enabled the release of the gas bubbles without introducing atmospheric air.

In oxic cores, oxygen consumption in the overlying water was then measured by recording the decrease of the oxygen concentration overnight (minimum of 3 h). This was followed by first sampling of the overlying water. Approximately 30 ml of the overlying water was sampled four times during a 14-day period. Water samples were analysed for DOC, UV_{254}, CH_4, NH_4^+, NO_3^-, PO_4^{2-}, Fe and Mn. Oxygen, pH and temperature were measured in the overlying water at the time of sampling. The sampled water volume was replaced by bottom water which was kept in separate brown bottles at in situ conditions (temperature and oxygen). This water was the same water that was used for the controls (see below). Therefore, the mean water quality of the controls was used to correct for the sample replacement in both controls and sediment cores. For anoxic experiments, the anoxic water was used to replace the sample water. Controls were prepared by incubating hypolimnion water in bottles. They were stirred before sampling and then sampled and analysed the same way as the sediment cores. This was done to account for changes that might occur in the water itself which are not influenced by sediment. A fifth control bottle was prepared specifically for control measurement of oxygen consumption. Previous experiments had shown that oxygen consumption in water was very slow such that the time frame used in sediment core oxygen consumption would be too short to measure oxygen consumption in water. The oxygen control bottle was measured for oxygen at the start and the end of the experiments.

To prevent oxygen contamination, sampling of the overlying water in anoxic cores was done using the concurrent withdrawal and replacement of the sample. This involved filling a syringe with replacement water (volume should be more than sample volume) and connecting this syringe to the short port (the one extending to the water surface) and taking the sampling syringe and connecting it to the long port (the one extending into the water column). The sample was collected by opening both ports and withdrawing the required sample volume, and as the sample was withdrawn, the syringe with replacement water was emptied into the core.

In oxic experiments, the levels of oxygen were maintained at in situ levels by occasional bubbling (2–3 days) using an air pump. For oxic experiments, NH_4^+ and pH were measured inside the cores by inserting the respective electrodes in the core, while in anoxic experiments, as a measure to prevent oxygen contamination, NH_4^+ and pH were measured in the sample volume.

Oxygen micro profiles were measured using a Clark-type microsensor with a tip diameter of 100 μm connected to a motor-driven micromanipulator (Unisense, Denmark). Since the water column was too high to reach the sediment surface, the standard O_2 sensor holder was elongated using a plastic tube. Vertical profiles of oxygen consumption were calculated using the software tool PROFILE (Berg et al. 1998).

2.4 Analytics

Dissolved organic carbon samples (12 ml) were filtered through pre-combusted (450 °C) GFF filters into pre-combusted (550 °C) brown glass vials before being analysed using a total organic carbon analyser (DIMATOC 2000; Dimatec Analysentechnik GmbH, Germany). Ultraviolet absorbance at 254 nm was analysed photometrically in the same samples using a quartz cuvette (Hach Lange DR 500; Hach Lange, Germany). Methane samples (1 ml) were injected into 10-ml glass flasks which had been prefilled with 200 μl of 1 M hydrochloric acid, closed with a rubber septum and aluminum crimp and flushed with argon/nitrogen gas for 5 min. The headspace was then analysed using a gas chromatograph (SRI, USA). Ammonium was measured using an ammonium ion-selective electrode with a separate lithium acetate reference electrode (ELIT 8051 and ELIT 003n; Nico2000 Ltd., UK). Samples for NO_3^-, SO_4^{2-}, Fe and Mn were filtered through a 0.2-μm syringe filter. NO_3^- and SO_4^{2-} (1.5 ml) were analysed by ion chromatography (DIONEX ICS-3000; DIONEX, Germany). Iron and manganese (1.5 ml) were analysed using an inductively coupled plasma mass spectrometer (Agilent 7500c ICP-MS; Agilent, Germany). PO_4^{2-} (1 ml) was analysed photometrically (Cary 60 UV/Vis spectrophotometer; Agilent, Malaysia).

2.5 Flux calculation and statistics

To correct for sample replacement, actual concentrations were calculated by factoring in the volume and concentration of the sample replaced. Assuming a linear relationship in the solute concentration change overtime, we determined the fluxes by subtracting the rates of change of solute concentration in controls from that of the sediments. The difference was multiplied by the volume of water in the core and divided by the sediment core surface area. Positive fluxes indicate efflux from sediment into water, while negative fluxes indicate influx from water into sediment.

All statistical analyses were done using SPSS, version 22. To determine the detection limit of our flux measurements (the smallest detectable flux), the analytical method detection limits were multiplied by 2 (factor for 95 % confidence interval) and the result was considered the smallest detectable concentration change between beginning and end of incubation. The smallest detectable flux (mmol m^{-2} day^{-1}) in the sediment cores was calculated by multiplying the minimum concentration change by the overlying water volume and dividing by the sediment core surface area and duration of incubation (Table 1). For the control bottles, detectable rates of change in concentration (mmol l^{-1} day^{-1}) were calculated by multiplying the analytical method detection limit by 2 divided by the duration of incubation. A one-sample *t* test was conducted to determine whether incubation fluxes were significant from zero. All fluxes significantly different from zero were run through a second one-sample *t* test with the test value being the flux detection limit. All fluxes not significantly different

Table 1 Mean sediment-water fluxes and standard deviation (*n*= 4) of various dissolved compounds at two sites in Hassel pre-dam in November 2013 in (mmol m^{-2} day^{-1})

Substance	Detection limit water (µmol l^{-1} day^{-1})	Detection limit flux[a] (cores) (mmol m^{-2} day^{-1})	Shallow site (oxic) (mmol m^{-2} day^{-1})	Deep site (anoxic) (mmol m^{-2} day^{-1})
O_2			−13.02±1.8	
DOC	5	1.25	<dl	2.31±0.66
NH_4-N	1	0.25	<dl	0.93±0.55
Fe	0.1	0.02	<dl	2.07±0.37
Mn	0.1	0.02	−0.02±0.01	0.27±0.02
SO_4^{2-}	1.3	0.33	0.46±0.03	−0.99±0.26
PO_4^{2-}	0.2	0.04	<dl	0.15±0.03
NO_3-N	3.3	0.83	−1.70±0.25	<dl[b]
CH_4	0.03	0.01	<dl[b]	1.41±0.19

Temperature was 5.2 °C. Negative fluxes are directed from the water into the sediment

dl detection limit

[a] Detection limit flux for a 9-cm-diameter core with overlying water height of 25 cm

[b] Concentration in the water below detection limit

from the detection limit flux were considered to be below the detection limit.

3 Results and discussion

3.1 Oxygen

Although great care was taken to remove all air bubbles in the field, most of the cores contained some bubbles upon arrival in the laboratory. These bubbles probably originated from air trapped in the crack between the stirring head and the outer wall of the core tube. The presence of bubbles during the O_2 flux measurements led to unreliable results because of the O_2 from the bubbles dissolves in the water. In fact, the dissolved oxygen concentration was increasing in the presence of bubbles (Fig. 2a). After removal of all bubbles, similar rates of linear oxygen consumption were observed across each replicate (Fig. 2b). Thus, before starting O_2 flux measurements, all cores have to be checked carefully and all bubbles have to be eventually removed.

Sediment cores from the anoxic hypolimnion, on the other hand, always contained between 4 and 13 % oxygen in the overlying water upon arrival in the laboratory. Although great care was taken to minimise the contact to the atmosphere, without using an anaerobic chamber, it was not possible to exclude oxygen completely during handling of these cores. Some oxygen contamination was also observed in other studies but not considered important (Hammond et al. 2004). Oxygen contamination of cores may oxidise reduced substances, leading to their precipitation. However, there was no relation observed between oxygen contamination and start concentrations of different solutes, e.g. Fe. Thus, oxygen contamination did not change the chemical composition of the overlying water. Furthermore, low oxygen concentrations should have only minor effects on the sediment, since with a diffusive boundary layer of 300 µm (Fig. 4), oxygen penetration into the sediment would probably be less than 100 µm. Oxygen contamination also has the potential to inhibit obligate anaerobes like methanogens. However, we have no hints on inhibition of methanogenesis since methane was produced in all anoxic cores without a lag phase.

Before incubation was started, oxygen was removed by gently bubbling the water with a mixture of N_2 and CO_2. The addition of CO_2 to the gas stream is essential to keep the pH constant. Bubbling with pure N_2 would drive out dissolved CO_2 and resulted in a pH increase of more than 1 pH unit (data not shown). Eventually, all remaining traces of oxygen were rapidly removed by sediment respiration.

We recommend keeping the height of the water column between 15 and 20 cm in order to optimise the sediment surface to water volume ratio as well as the mixing rate. A longer water column might result in less efficient mixing, while a too small water column might provoke resuspension. The resulting water volume of about 1 l is, on the one hand, small enough to speed up concentration changes and is, on the other hand, not substantially affected by the sampling volume (30 ml).

It is known that the stirring rate affects O_2 consumption in sediments due to its effect on diffusive boundary layer thickness. This effect is especially relevant in situations with high oxygen consumption rates, when O_2 consumption in the sediment becomes transport limited (Glud 2008). However, at low sediment oxygen demand, the O_2 flux is rather independent from the bottom shear velocity, providing some minimum water movement (Higashino et al. 2004; Beutel et al. 2006). We consider transport limitation not important in the case of our low DOC fluxes.

If oxygen consumption measurements were began directly upon arrival in the laboratory, we always observed an initial

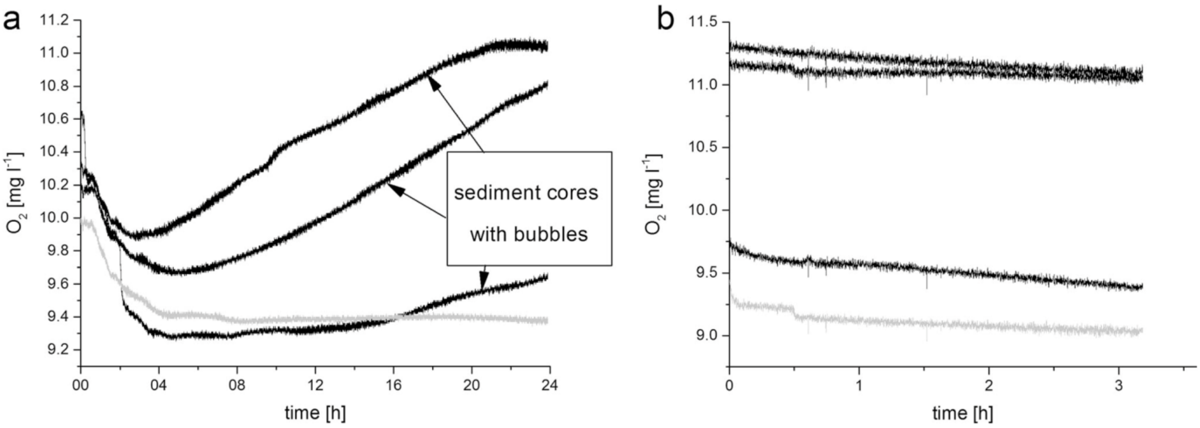

Fig. 2 Temporal change of the oxygen concentration during four replicate oxygen flux measurements in the presence (**a**) and absence (**b**) of bubbles (Hassel pre-dam, April 2013)

fast drop in the oxygen concentration (Fig. 2a). After about 4 h, this effect levelled out and a constant oxygen consumption rate was reached. A possible explanation for this initial elevated O_2 consumption is that during transportation, reduced solutes from the pore water were mixed into the water which were then oxidised. Thus, it is essential to allow a pre-incubation after transportation of at least 4 h.

Typical oxygen fluxes were in the range of 10 to 20 mmol m^{-2} day^{-1} (concentration change in the water 0.06 to 0.12 mmol l^{-1} day^{-1}) as exemplified by the data from November 2013 (Table 1). These are typical values for lake sediments (Müller et al. 2012). Compared to that, oxygen consumption rates in the control bottle was about 1 order of magnitude lower (−0.001 mmol l^{-1} day^{-1}). Thus, oxygen consumption in the free water was small but should be considered.

An oxygen flux of 18 mmol m^{-2} day^{-1} would completely remove all dissolved oxygen from 100 % saturated 2 l of water within 8 and 6 days at a water temperature of 5 and 15 °C, respectively. Thus, we periodically checked the oxygen concentration during the 14-day incubation. Every 2–3 days, we bubbled the cores with air to restore the original concentration. So, it was possible to keep the O_2 concentration reasonably constant during the incubation (Fig. 3(c))

In April 2013, when the entire water column contained oxic water, we measured oxygen microprofiles in the cores from a Hassel pre-dam (Fig. 4). The diffusive O_2 flux calculated from these microprofiles was 16.6±1 mmol m^{-2} day^{-1}, while the flux determined in the sediment core incubations was 18±4.2 mmol m^{-2} day^{-1}. The fact that the total flux (as determined by the core incubation) was equal to the diffusive flux (as determined from the microprofiles) shows that flux enhancement by bioturbation did not occur in our reservoirs. This is consistent with the fact that *chironomid* larvae were rarely observed in the sediment cores. The analysis of the microprofile also shows that rates of benthic respiration decreased with sediment depth (dotted line in Fig. 4). Thus, O_2 consumption was probably dominated by aerobic respiration of organic matter and not by the oxidation of reduced solutes diffusing into the oxic sediment layer from below (Hargrave 1969).

3.2 UV_{254} as a proxy for DOC

In plotting all UV_{254} data against the DOC concentration that was measured in the same samples, it becomes clear that the relation between the two parameters was site specific (Fig. 5). There were significant correlations for the samples from the Muldenberg pre-dam and from the shallow (oxic) site at the Hassel pre-dam (r=0.97 and 0.79, respectively). Calculations of DOC fluxes from UV_{254} data using the calibration shown in Fig. 5 result in the mean DOC fluxes of −3.2±1.9 and 26.3±14.6 mmol m^{-2} day^{-1} for the Muldenberg cores in April and June, respectively, which is not statistically different to the fluxes determined from direct DOC analysis (−2.0±1.6 and 18.7±8.6 mmol m^{-2} day^{-1}) (t test).

At the deep (anoxic) site of Hassel pre-dam, however, the correlation between UV_{254} and DOC was poor (r=0.6). Obviously, at that site, either the proportion of optical active DOC was rather variable or other solutes contribute to UV absorption. It is well known that iron contributes to UV absorption in natural waters (Weishaar et al. 2003; Maloney et al. 2005; Xiao et al. 2013). A plot of UV_{254} values against the concentrations of Fe or Mn (Fig. 5) shows some significant (p<0.05) positive correlation (at 0.01 level) between Fe and UV_{254}, especially in the samples from the anoxic site. Thus, in samples containing elevated concentrations of iron, which is typical for anoxic hypolimnic water, UV_{254} cannot be used as a proxy for DOC. The apparent correlation between Mn and UV_{254} was probably a pseudo-correlation caused by a highly

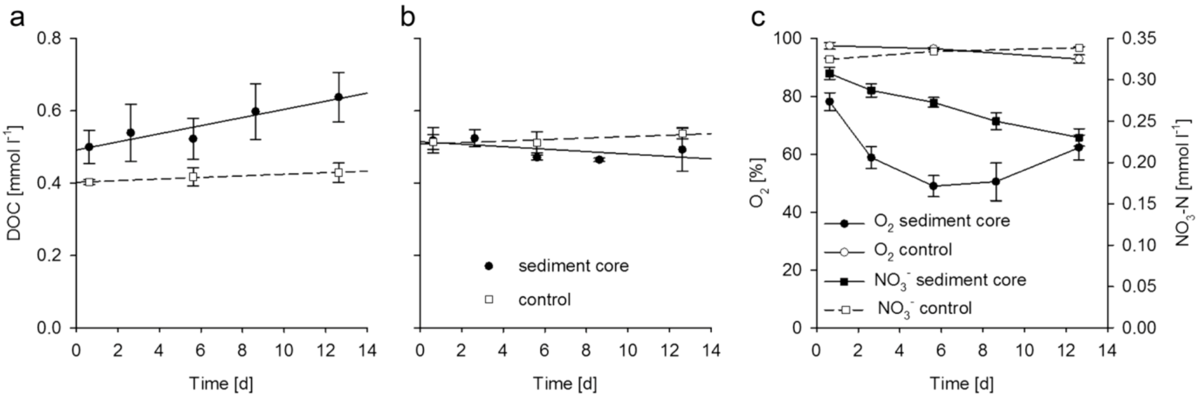

Fig. 3 Dissolved organic carbon, oxygen and nitrate concentration during incubation (November 2013) for Hassel shallow (oxic; **b**, **c**) and Hassel deep (anoxic; **a**) in sediment cores and control

significant correlation between Mn and Fe concentration (r= 0.603 at Hassel deep site).

Interestingly, the difference between DOC/UV$_{254}$ relations was bigger between two sampling sites in the same reservoir than between different reservoirs. Thus, it is not sufficient to establish one calibration curve for a given water body. We suggest that UV$_{254}$ can be used as a proxy for DOC at oxic sites after establishing a site-specific calibration.

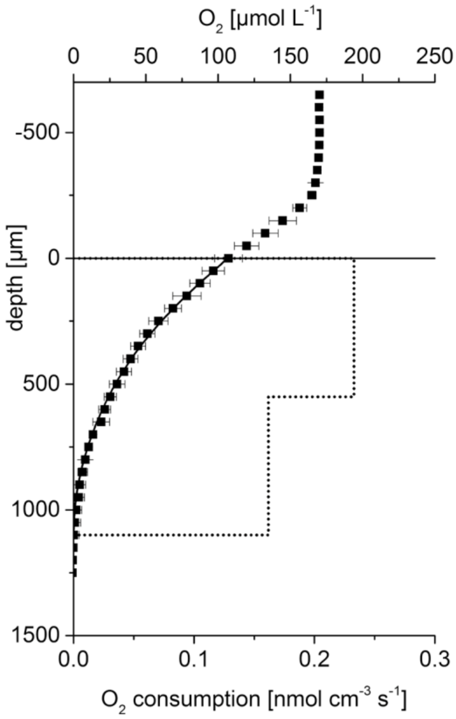

Fig. 4 Oxygen microprofile in a sediment core from the deep site at Hassel pre-dam measured at 4 °C (mean and SD of three replicates). The *dotted lines* show the oxygen consumption rates calculated with software tool PROFILE

3.3 DOC and other fluxes

Using our set-up, we were able to measure the fluxes of several dissolved solutes simultaneously (Table 1). In the controls, changes of DOC were always below the detection limit. Changes of other solutes in the controls were also below the detection limits with the exception of ammonium and manganese at the deep site which slightly increased. Thus, in our case, controls did not affect our flux calculations. Controls are mandatory but might be conducted with less effort, e.g. analysis only at the start and end of the experiment or alternatively measuring only UV$_{254}$ if the DOC and UV$_{254}$ correlation for the site is acceptable.

At the shallow oxic site, the flux of DOC between sediment and water was not significantly different from zero, while at the deep anoxic site, the sediment was a source of DOC. Regardless of the mechanism involved, our results show that the DOC flux is probably influenced by the redox conditions at the sediment-water interface. Similar to DOC, also the fluxes of other solutes were higher under anoxic conditions (Table 1). It is well known that oxygen is a major regulator of benthic solute fluxes. Table 1 shows higher fluxes of Fe, DOC and P under anoxic conditions. Since the flux pattern was similar for DOC, Fe and P, we suspect the same mechanism to be responsible. The reductive dissolution of iron is one of the mechanisms known to trigger internal P loading from sediments (Hupfer and Lewandowski 2008). It has been suggested that reductive dissolution of Fe and release of DOC which had been adsorbed to the oxidised Fe also affects the DOC flux at the sediment-water interface (Skoog et al. 1996).

The sulfate uptake under anoxic conditions can be interpreted as an aerial sulfate reduction rate. The observed rate of 1 mmol m^{-2} day^{-1} is typical for a eutrophic lake (Holmer and Storkholm 2001) and highlights the significance of sulfate reduction for organic matter mineralisation not only in marine but also in freshwater sediments. Considering the electron balance of the different processes (eight electrons per

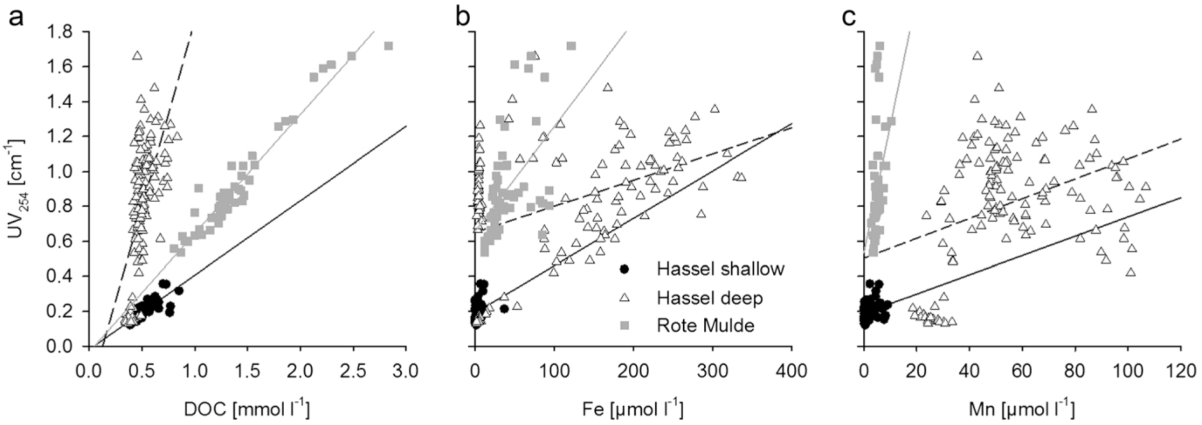

Fig. 5 Ultraviolet absorbance at 254 nm (UV_{254}) plotted against *a* dissolved organic carbon (*DOC*), *b* iron (*Fe*) and *c* manganese (*Mn*) concentration in headspace water of incubated sediment cores. UV_{254}/DOC, UV_{254}/Fe and UV_{253}/Mn correlations were significant at 0.01 level for all sites. $n=128$ for both Hassel shallow and deep and $n=52$ for Rote Mulde pre-dam

sulfate, four electrons per CH_4, one electron per Fe) (Wendt-Potthoff et al. 2014), sulfate reduction appeared to be the most important process of organic matter mineralisation under anoxic conditions. Under oxic conditions, organic matter mineralisation was dominated by aerobic respiration and, to a lesser extent, by denitrification, as indicated by the negative flux of nitrate (Table 1).

The redox conditions at the sediment surface are known to be crucial for the benthic fluxes of other solutes like, for example, CH_4. Methane is produced in the anoxic sediment and then diffuses to the oxic surface sediment where most of it is oxidised by methanotrophic bacteria (Frenzel et al. 1990). A redox dependency of the flux seems to exist also for DOC. Thus, it is important to keep redox conditions constant during the incubation in such environments. This was successfully done by periodic bubbling with air (Fig. 3(b)). This approach is not as elegant as automatic oxygenation set-ups (Sommer et al. 2008) but provides a simple practical solution to keep O_2 between 50 and 100 % saturation.

The standard deviations of our replicates show that four replicates were sufficient to cover the natural variability between different cores. Typical shallow site standard deviations from four replicate cores were 39, 14 and 16 % for the fluxes of DOC, O_2 and Fe, respectively. Our data suggest that small-scale heterogeneity of the DOC flux might be higher than that of Fe, Mn, P and SO_4^{2-}. A particularly high variability was observed for the flux of NH_4^+, which is probably linked to the small-scale heterogeneity of organic matter mineralisation. For a typical lake situation, we recommend the use of four replicates, but even three replicates would have produced reliable results in our case. The fluxes of the different solutes differed over several orders of magnitude (Table 1). This highlights the need to adjust the incubation time to the parameter of interest. Although, in our case, shortening the incubation time to 10 days would probably have produced reliable results, we recommend a 2-week incubation as a good compromise to measure the flux of different solutes simultaneously.

4 Conclusions

We presented a method allowing a reliable measurement of the flux of DOC between sediment and water in lakes. DOC fluxes appeared to be small, requiring incubation for 2 weeks. Two periods of incubation, one fast for oxygen flux measurement followed by a long incubation, allow the simultaneous quantification of the flux of O_2, DOC and other solutes. We find the method to be particularly effective in addressing crucial aspects of sediment core incubation, mixing of overlying water and handling of anoxic experiments. Specific UV absorption (SUVA) was site specific and influenced by dissolved iron. UV_{254} can be used as a proxy for DOC under oxic conditions, but a site-specific calibration has to be done.

The method also allows the measurement of the fluxes of other dissolved substances. Incubation time and number of replicates may be adapted according to the magnitude of the particular flux, the precision of the analytical method and existing small-scale spatial variability.

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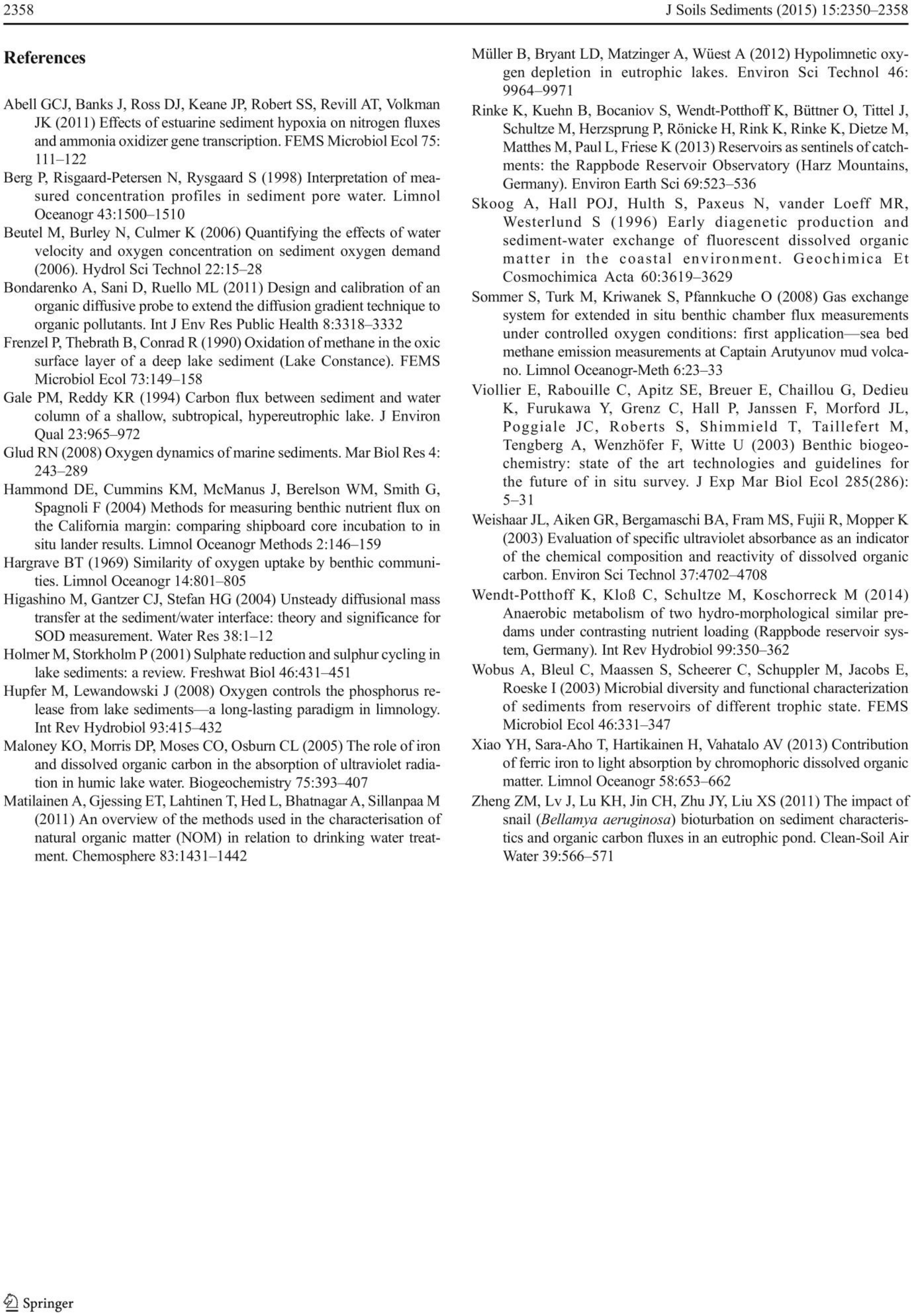

References

Abell GCJ, Banks J, Ross DJ, Keane JP, Robert SS, Revill AT, Volkman JK (2011) Effects of estuarine sediment hypoxia on nitrogen fluxes and ammonia oxidizer gene transcription. FEMS Microbiol Ecol 75: 111–122

Berg P, Risgaard-Petersen N, Rysgaard S (1998) Interpretation of measured concentration profiles in sediment pore water. Limnol Oceanogr 43:1500–1510

Beutel M, Burley N, Culmer K (2006) Quantifying the effects of water velocity and oxygen concentration on sediment oxygen demand (2006). Hydrol Sci Technol 22:15–28

Bondarenko A, Sani D, Ruello ML (2011) Design and calibration of an organic diffusive probe to extend the diffusion gradient technique to organic pollutants. Int J Env Res Public Health 8:3318–3332

Frenzel P, Thebrath B, Conrad R (1990) Oxidation of methane in the oxic surface layer of a deep lake sediment (Lake Constance). FEMS Microbiol Ecol 73:149–158

Gale PM, Reddy KR (1994) Carbon flux between sediment and water column of a shallow, subtropical, hypereutrophic lake. J Environ Qual 23:965–972

Glud RN (2008) Oxygen dynamics of marine sediments. Mar Biol Res 4: 243–289

Hammond DE, Cummins KM, McManus J, Berelson WM, Smith G, Spagnoli F (2004) Methods for measuring benthic nutrient flux on the California margin: comparing shipboard core incubation to in situ lander results. Limnol Oceanogr Methods 2:146–159

Hargrave BT (1969) Similarity of oxygen uptake by benthic communities. Limnol Oceanogr 14:801–805

Higashino M, Gantzer CJ, Stefan HG (2004) Unsteady diffusional mass transfer at the sediment/water interface: theory and significance for SOD measurement. Water Res 38:1–12

Holmer M, Storkholm P (2001) Sulphate reduction and sulphur cycling in lake sediments: a review. Freshwat Biol 46:431–451

Hupfer M, Lewandowski J (2008) Oxygen controls the phosphorus release from lake sediments—a long-lasting paradigm in limnology. Int Rev Hydrobiol 93:415–432

Maloney KO, Morris DP, Moses CO, Osburn CL (2005) The role of iron and dissolved organic carbon in the absorption of ultraviolet radiation in humic lake water. Biogeochemistry 75:393–407

Matilainen A, Gjessing ET, Lahtinen T, Hed L, Bhatnagar A, Sillanpaa M (2011) An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. Chemosphere 83:1431–1442

Müller B, Bryant LD, Matzinger A, Wüest A (2012) Hypolimnetic oxygen depletion in eutrophic lakes. Environ Sci Technol 46: 9964–9971

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

Skoog A, Hall POJ, Hulth S, Paxeus N, vander Loeff MR, Westerlund S (1996) Early diagenetic production and sediment-water exchange of fluorescent dissolved organic matter in the coastal environment. Geochimica Et Cosmochimica Acta 60:3619–3629

Sommer S, Turk M, Kriwanek S, Pfannkuche O (2008) Gas exchange system for extended in situ benthic chamber flux measurements under controlled oxygen conditions: first application—sea bed methane emission measurements at Captain Arutyunov mud volcano. Limnol Oceanogr-Meth 6:23–33

Viollier E, Rabouille C, Apitz SE, Breuer E, Chaillou G, Dedieu K, Furukawa Y, Grenz C, Hall P, Janssen F, Morford JL, Poggiale JC, Roberts S, Shimmield T, Taillefert M, Tengberg A, Wenzhöfer F, Witte U (2003) Benthic biogeochemistry: state of the art technologies and guidelines for the future of in situ survey. J Exp Mar Biol Ecol 285(286): 5–31

Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37:4702–4708

Wendt-Potthoff K, Kloß C, Schultze M, Koschorreck M (2014) Anaerobic metabolism of two hydro-morphological similar predams under contrasting nutrient loading (Rappbode reservoir system, Germany). Int Rev Hydrobiol 99:350–362

Wobus A, Bleul C, Maassen S, Scheerer C, Schuppler M, Jacobs E, Roeske I (2003) Microbial diversity and functional characterization of sediments from reservoirs of different trophic state. FEMS Microbiol Ecol 46:331–347

Xiao YH, Sara-Aho T, Hartikainen H, Vahatalo AV (2013) Contribution of ferric iron to light absorption by chromophoric dissolved organic matter. Limnol Oceanogr 58:653–662

Zheng ZM, Lv J, Lu KH, Jin CH, Zhu JY, Liu XS (2011) The impact of snail (*Bellamya aeruginosa*) bioturbation on sediment characteristics and organic carbon fluxes in an eutrophic pond. Clean-Soil Air Water 39:566–571

Chapter 4a: Benthic dissolved organic carbon fluxes in a drinking water reservoir

Tallent Dadi, Kurt Friese, Katrin Wendt-Potthoff, Matthias Koschorreck

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Image: Hassel shallow site sediment cores at the end of incubation, showing a *chironomid* burrow (left core). Image by Tallent Dadi

Overview

Increasing DOC in surface waters in the northern hemisphere has led to intensified research on DOC. The research aims to gain better understanding of the causes and processes involved, in order to find solutions to the social, health and ecological impacts arising therefrom. This publication makes a contribution to the research on DOC and focus on benthic exchange and relevant processes in a drinking water reservoir. Batch core sediment incubation was used to get plausible benthic DOC fluxes. The publication also highlights the importance of redox conditions and temperature as the main drivers in benthic DOC exchange. Furthermore it identifies mobilization and immobilization of DOC from/by Fe minerals as an important mechanism regulating benthic DOC exchange. The findings are interesting, in light of envisaged global warming, which will trigger anoxia, through both stronger stratification and increased productivity in the standing water bodies.

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Benthic dissolved organic carbon fluxes in a drinking water reservoir

Tallent Dadi,* Kurt Friese, Katrin Wendt-Potthoff, Matthias Koschorreck
Department of Lake Research, UFZ - Helmholtz Centre for Environmental Research, Magdeburg, Germany

Abstract

The trend of increasing dissolved organic carbon (DOC) in surface waters motivated us to gain a mechanistic understanding of DOC exchange at the sediment water interface in lakes. We quantified seasonal DOC and solute fluxes under different redox conditions, in a small drinking water reservoir using sediment core incubations. Processes governing benthic DOC exchange were microbial production of DOC and interaction with mineral surfaces. Mobilization of DOC in anoxic sediments seemed to be closely linked to reductive dissolution of ferric minerals as shown by the strong positive correlation ($r^2 = 0.99$) between DOC and Fe fluxes. Oxidized surface sediments were an efficient DOC trap where DOC was bound to ferric minerals. Redox conditions appeared to be the primary regulator of the DOC exchange, resulting in sedimentary uptake of DOC (-1.8 mmol m^{-2} d^{-1}) only under oxic conditions. DOC production was regulated by temperature, leading to higher DOC fluxes (up to 2.4 mmol m^{-2} d^{-1}) in summer. The sediment was a net sink of DOC (-0.2 tonnes yr^{-1}) but this was small compared with the annual DOC load (15 tonnes yr^{-1}) of the reservoir. However, the benthic DOC flux was about 10–20% of the dissolved carbon flux at the sediment–water interface, making it a significant process in the lake internal carbon cycle. Climate change is supposed to promote reducing conditions at the bottom of lakes, which might increase benthic DOC production in the future.

Levels of dissolved organic carbon (DOC) have been increasing in many surface waters in the northern hemisphere (Freeman et al. 2001a; Monteith et al. 2007). This affects aquatic ecosystems due to e.g., altered light climate (Maloney et al. 2005) or increased greenhouse gas production (Peura et al. 2014) and a variety of harmful or beneficial effects on aquatic organisms (Steinberg et al. 2006). Increasing DOC also causes problems for drinking water production, due to increasing treatment costs and the formation of toxic trihalomethanes (THMs) during disinfection (Galapate et al. 2001; Gough et al. 2014).

The concentration of DOC in lakes and reservoirs is a combined effect of net inflow, internal processes and net outflow. Rising DOC trends in lakes have mainly been attributed to increased input from the catchment (Kortelainen 1993; Brothers et al. 2014). However, internal processes like algal production and consumption of DOC in the water column (Van Den Meersche et al. 2004; Rodriguez et al. 2013), DOC exchange with the sediment through diffusion from porewater (Burdige and Homstead 1994), and sediment resuspension (Biddanda and Cotner 2002; Koelmans and Prevo 2003) can potentially contribute to DOC increase in lakes. To understand DOC concentration dynamics in the lake, detailed understanding of the aforementioned lake internal DOC cycling processes and interactions is crucial. While several studies addressed the turnover of DOC in lake water (Bastviken et al. 2004; Guillemette and Del Giorgio 2012), less is known about the exchange of DOC between water and sediment.

While net sedimentation of particulate organic matter is a one way process directed from the water toward the sediment, the flux of DOC is a two way process accomplished by diffusion, advection and sediment resuspension. Thus the sediment can be either a source or a sink of DOC. The few existing studies show that sediments are probably a DOC source (Koelmans and Prevo 2003; Downing et al. 2008). Microbial degradation of particulate organic matter typically results in elevated DOC concentrations in the sediment porewater (Boto et al. 1989; Burdige et al. 1992; Alperin et al. 1999; Sachse et al. 2001) and from this it can be predicted that sediments are a DOC source by virtue of the concentration gradient. Depending on the availability of electron acceptors, various microbial processes, probably most important aerobic respiration, sulfate reduction, and methanogenesis, are involved in benthic DOC turnover. However, the fate of the DOC will also be influenced by the DOC quality and bioavailability. Since some dissolved organic molecules require molecular oxygen for complete degradation (Hansen and Blackburn 1991; Freeman et al. 2001b), we can postulate a higher production of DOC under anoxic conditions. Regardless of the process involved, if

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*Correspondence: tallent.dadi@ufz.de

microbial processes are controlling the DOC exchange at the sediment water interface, we expect the DOC flux to depend on temperature (Bergström et al. 2010; Gudasz et al. 2010, 2012). We can also expect some relation between the flux of DOC and substances indicating microbial processes, like O_2 and SO_4^{2-}. Sulfate reduction contributes to mineralization of organic carbon and is also linked to immobilization of reactive iron through formation of iron sulfides (Roden and Edmonds 1997; Taillefert et al. 2002).

In the presence of mineral particles, however, the concentration of DOC is not only influenced by metabolic processes, but also by interaction with mineral surfaces. Iron minerals are well known to adsorb DOC (Tipping 1981; Davis 1982) and the normally observed accumulation of DOC in the hypolimnion during stratification is closely linked to an accumulation of iron (Tipping and Woof 1983). Recent studies have also linked adsorption of organic carbon to Fe mineral surfaces to the preservation of organic carbon (Lalonde et al. 2012; Barber et al. 2014). In marine sediments it has been shown that the flux of fluorescent DOC was driven by adsorption processes which were controlled by iron redox state (Skoog et al. 1996; Skoog and Arias-Esquivel 2009). The same process seems to be relevant also in lakes (Luider et al. 2003; Brothers et al. 2014). Iron redox state mainly depends on oxygen availability with the soluble ferrous more stable under anoxia and the particulate ferric more stable under oxic conditions. Iron speciation is also influenced by pH, ionic strength, temperature and presence of organic chelators (Jones et al. 1993; Maranger and Pullin 2003). Anoxia is a common phenomenon in lakes which occurs mostly in summer and is well studied, especially its effects on release of phosphorus bound to ferric iron minerals (Mortimer 1942; Hupfer and Lewandowski 2008). Even though little is known about DOC exchange at the sediment water interface, we postulate that DOC is released after anoxia triggered reductive dissolution of iron minerals. In line with this postulation DOC and phosphorus release and or adsorption should follow a similar trend.

Our objective was to clarify the direction, magnitude, and regulation of the benthic DOC flux. To discriminate between regulating factors, we studied the seasonal change of the benthic flux of different solutes at two contrasting sites in a reservoir by sediment core incubations. We hypothesize that the benthic DOC flux is regulated both by the microbial degradation of organic matter (production) and adsorption/desorption from iron minerals. We therefore, expect temperature to increase DOC production and reducing conditions to release DOC associated with iron minerals.

Materials and methods

Site description

Hassel pre-dam is located in the Harz Mountains (51.74° N, 10.89° E), in central northern Germany. It is part of the Rappbode Reservoir System and was built in 1960 to reduce the sediment and phosphorus load into the Rappbode Reservoir (Rinke et al. 2013; Friese et al. 2014). The pre-dam has a maximum and mean depth of 14 m and 5 m, respectively. It has a surface area of 0.26 km^2 and is approximately 2 km in length and has a mean water retention time of 65 d. Pre-dams are characterized by a constant water level, because water outflow is always over the dam wall. Thus, they are similar to natural lakes rather than to classical reservoirs.

The dimictic pre-dam develops an anoxic hypolimnion during summer stratification (Wendt-Potthoff et al. 2014). Two representative sampling sites were selected for this study on the basis of seasonal temperature and redox variation. The shallow sampling site (3.5 m depth), which is near the inflow is oxic throughout the year and the water temperature ranges from 4°C in winter to a summer peak of 20°C while the deep sampling site (13 m depth), which is near the outflow to the main reservoir has a constant temperature (4–6°C) and is anoxic during summer stratification.

Field sampling

At each site and sampling date, four replicate sediment cores were taken in 9 cm diameter and 60 cm long clear PVC tubes, using a gravity corer (UWITEC, Mondsee, Austria). The water level height in the cores was on average 24 cm, which translates to a volume of 1.4 L. The cores were immediately covered with specially designed Plexiglas sediment core covers. The core covers had three O-rings to be air and water tight. They also had a 2 mm diameter opening for oxygen sensors (which is closed by a silicon stopper when not in use), 20 mm diameter opening for pH and ammonium electrode. In addition they also had two (4 mm diameter) openings (closed by a two-way stop cock). One opening was for sample taking and gas bubbling (it had an extended and adjustable silicon tube) and the other for gas release during bubbling. The covers had an inbuilt motor system connected to a magnet with a second magnet attached to the inside of the cover to complete the stirring system. The covers also had a detachable battery unit for power when in the field. For a detailed description of the sediment core cover design refer to Dadi et al. (2015). The cores were filled to the top with bottom water and all bubbles were removed. The battery powered stirring system avoided potential stratification during transport. Sediment cores were transported to the laboratory in insulated boxes so as to keep them at in situ temperature. Bottom water was sampled using a standard 2-L water sampler (Hydrobios, Kiel, Germany) at approximately 0.5 m above the sediment. Bottom water samples were collected for use in control incubations and replacement of sampling water during core incubation. Sediment cores were collected in 2013; April, June, July, September, October, and November. The April samples were taken the week after ice off.

Sediment incubation

Sediment cores were incubated in a controlled temperature climate chamber. The temperature of the climate rooms was adjusted to the in situ temperature. Cores were wrapped with aluminum foil to prevent light penetration and incubated for 14–31 d. Sediment cores were allowed to stand for one night to allow for acclimatization and to measure oxygen consumption in the overlying water, which was done using optodes (Pyroscience, Aachen, Germany). The overlying water of the cores was sampled every 3 d to analyze DOC, total inorganic carbon (TIC), CH_4, NH_4^+, NO_3^-, soluble reactive phosphorus (SRP), SO_4^{2-}, Fe, and Mn. Controls were prepared by incubating bottom water in bottles which were sampled and analyzed the same way as the sediment cores. This was done to account for changes that might occur in the water itself but which are not influenced by sediment. Sampled water (25 mL) in both core and controls was replaced by bottom water from the sampling site. The sampled volume was approximately 2% of the total water volume in the cores.

In oxic experiments the levels of oxygen were maintained at in situ levels by occasional bubbling using an air pump. In anoxic experiments anoxic conditions were checked using an optode before the start of the experiment. When oxygen was detected the cores were bubbled with a mixture of nitrogen and carbon dioxide (99.96% N_2/0.04% CO_2) until they were anoxic. Mixed nitrogen and carbon dioxide gas was used to maintain the pH. Sampling of the overlying water in anoxic cores was performed using the concurrent withdrawal and replacement of the sample to prevent oxygen contamination. This was achieved by filling a syringe with 25 mL of anoxic hypolimnion water and attaching it to one of the sediment cover openings and then an empty syringe was fixed to the second opening. For detailed description of the incubation setup refer to Dadi et al. (2015).

Sediment resuspension and sectioning

To check whether oxidation and precipitation of reduced porewater compounds was involved in DOC consumption at the sediment water interface, sediment resuspension experiments were carried out soon after the last sampling of the incubation experiment. The resuspension was carried out manually by disturbing approximately the upper 1 cm sediment layer using a glass rod. For anoxic cores oxygen contamination was prevented by stopping the stirrers during the resuspension which was done within 30 s. After resuspension bubbles from the cores were removed and the cores were closed. The stirred cores were incubated for a period of 24 h. From prior turbidity tests we knew that turbidity of the overlying water in resuspended cores became constant after 18 h, hence a 24 h incubation period was chosen. After approximately 24 h the overlying water from the resuspended cores was sampled and analyzed like in the previous section.

After the resuspension experiment the sediment was sectioned in three layers (0–1, 1–3, 3–5 cm) and part of the sediment samples was used for porewater extraction and another part for water content and organic matter content analysis. Porewater was extracted by centrifugation at 3750 rpm for 15 min at the incubation temperature. The supernatant was collected and analyzed for DOC, TIC, CH_4, NO_3^-, SRP, SO_4^{2-}, Fe, and Mn.

Analytical methods

Samples for DOC were filtered into pre-combusted (550°C) brown glass vials through pre-combusted (450°C) GFF (Whatman GFF) filters. Dissolved organic carbon samples were analyzed by a TOC analyzer (DIMATOC 2000, DIMATEC Analysentechnik GmbH, Germany). Methane and TIC samples were prepared by injecting 1 mL sample into 10 mL glass vials which had been prefilled with 200 μL 1M hydrochloric acid, closed with a rubber septum and aluminum crimp, and flushed with argon/nitrogen gas for 5 min. Headspace gas samples were withdrawn for analysis by a gas chromatograph (SRI, U.S.A.). Ammonia was measured by an ammonium ion selective electrode with a separate lithium acetate reference electrode (ELIT 8051 & ELIT 003n, Nico2000 Ltd, UK). Samples for NO_3^-, SO_4^{2-}, Fe, and Mn were filtered using a 0.2 μm syringe filter. NO_3^- and SO_4^{2-}, (1.5 mL) were analyzed by ion chromatography (DIONEX ICS-3000, DIONEX, Germany). Fe and Mn (1.5 mL) were analyzed using an inductively coupled plasma mass spectrometer (Agilent 7500c ICP-MS, Agilent, Germany). SRP (1 mL) was analyzed photometrically (Laskov et al. 2007).

Sediment water content was determined by drying the sediment samples at 105°C and then determining the difference in sample weight before and after drying. Organic matter content was analyzed using the loss on ignition method (550°C, 2 h).

Oxygenation of anoxic sediments experiment

To test the influence of oxygen on the DOC flux, sediment cores were collected from the deep site in June 2013. At the time of collection the overlying water was anoxic. Four cores were incubated anoxically and the other set of four cores were incubated oxically, at a temperature of 4.2°C. The cores for the oxic incubation were initially bubbled with oxygen using an air pump. Oxygen level was monitored during the incubation period and the oxic cores were bubbled occasionally to maintain oxic conditions.

Sediment traps

Sediment traps were deployed at the shallow and deep sites to coincide with the sediment sampling. They were deployed for periods ranging between 1 months and 2 months. The settling material was collected in 1-L plastic bottles. In the laboratory, the material was left for at least 24 h to ensure the settling of the suspended particles. The supernatant water was then removed carefully and the

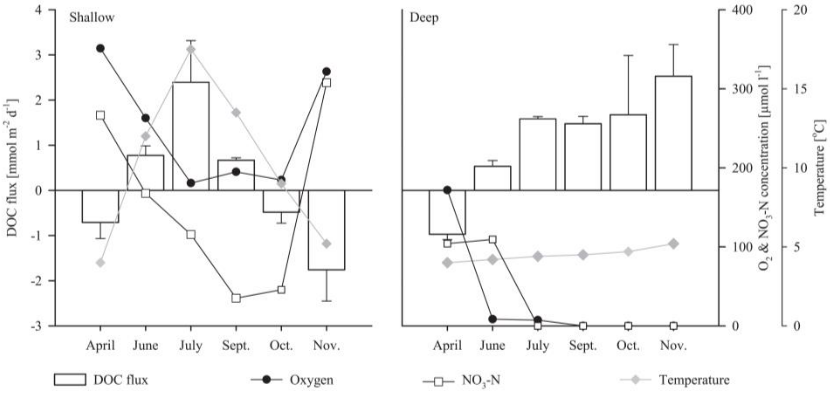

Fig. 1. Seasonal DOC flux, initial concentrations of oxygen and nitrate, and temperature at the sediment surface in shallow and deep site. Error bars represent standard deviation of four replicate cores.

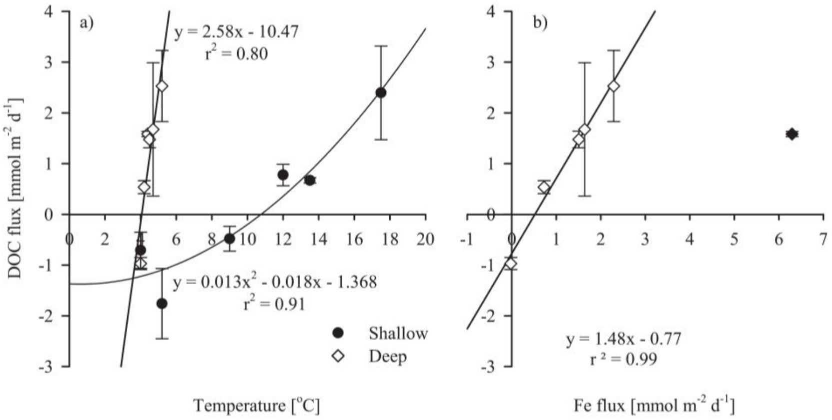

Fig. 2. Relationship of DOC fluxes to temperature and Fe flux: (**a**) DOC and temperature at shallow and deep site and (**b**) DOC and Fe at deep site. The dark symbol in (**b**) shows the flux in July directly after nitrate depletion, when the Fe flux was extraordinarily high. Error bars represent standard deviation of four replicate cores.

residue was centrifuged for 15 min at 3500 rpm in a cooled (8°C) centrifuge. Again, the supernatant water was discarded and the residue freeze-dried for further analyses. Total organic carbon was measured with an elemental analyzer according to DIN ISO 10694 (1996) after combustion of the sample material in a high temperature combustion unit at temperatures of 1150°C (vario EL cube; Elementar Analysensysteme Hanau, Germany). Samples were acidified before measuring by adding sulfuric acid to eliminate inorganic carbon if present.

Calculations

To calculate solute fluxes, actual concentrations were corrected for the sample replacement by factoring in the amount and concentration in the replaced water. Fluxes were calculated from the linear concentration change with time minus the rates of change of solute concentration in the controls multiplied by height of the water column in the cores. Positive fluxes are directed from the sediment into the water.

The effect of resuspension was calculated as the difference between the concentration before and after resuspension divided by the sediment core (9 cm diameter) surface area and expressed on per event basis.

To determine the relevance of the different electron acceptors, their fluxes were multiplied with solute specific factors: 4 for O_2, CH_4 and TIC, 5 for NO_3^-, 8 for SO_4^{2-}, 2 for Mn and 1 for Fe (Matthews et al. 2008; Wendt-Potthoff et al.

Table 1. Dissolved organic carbon flux Pearson's correlations with solute fluxes and concentrations for; all data, oxidized (O_2 and NO_3^-) and reduced conditions (no O_2 and NO_3^-). Please note: Table only shows data for which there was a significant correlation for at least one of the datasets. High non-significant correlations are highlighted in grey.

	DOC concentration/flux	All data *n* = 12	Oxic data *n* = 8	Anoxic data *n* = 4
O_2	Concentration	−0.59*	NS	.‡
NO_3-N	Concentration	−0.69*	NS	.‡
Mn	Concentration	0.65*	NS	0.91
SO_4^{2-}	Flux	−0.71†	NS	−0.99†
TIC	Flux	0.66*	NS	0.91
TIC	Concentration	0.67*	NS	NS
SRP	Flux	0.60*	NS	0.89
SRP	Concentration	NS	NS	−0.99†
NH_4-N	Concentration	NS	NS	0.90
Temp	Flux	NS	0.81*	0.96*
C sed.	Flux	NS	0.80*	NS

NS, not significant.
*Correlation is significant at the 0.05 level (two-tailed).
†Correlation is significant at the 0.01 level (two-tailed).
‡Concentration was zero.

2014). The solute specific factors are based on the common redox stoichiometry for the decomposition of organic matter.

To calculate the annual sediment carbon budget, we quantified the sediment area of the pre-dam overlain by anoxic and oxic water using biweekly measured pre-dam oxygen profiles (field data) and bathymetric data (echo sounding method). To determine the oxic DOC release, an equation showing the DOC temperature dependency from the sediment incubations (Fig. 2a) was applied to bottom temperatures obtained from biweekly pre-dam temperature profiles to get the DOC flux which was then then multiplied by biweekly pre-dam oxic area. The anoxic DOC release was calculated by multiplying the mean DOC flux for the anoxic period obtained from our sediment incubations by the biweekly pre-dam anoxic area from the oxygen profile data. The results of the biweekly oxic and anoxic carbon release/uptake for the whole year were summed to give the annual sediment carbon budget. In a similar way, total release of methane and TIC was calculated. The sum of DOC, TIC, and CH_4 release is the total flux of dissolved carbon at the sediment water interface. Carbon sedimentation was calculated by summing the product of the sedimentation rate of the shallow and deep sites, and the total shallow and deep surface areas.

Statistical tests were calculated using SPSS version 22.

Results

Seasonality of benthic fluxes

Redox conditions and temperature both changed with season in the Hassel pre-dam. The seasonal pattern of the benthic DOC flux was different between the two investigated sites (Fig. 1). In April, under oxic and low temperature conditions the sediment was a sink of DOC at both sites. Both the shallow and deep site exhibited a temperature dependent trend (Fig. 2a), however, the seasonal variation in temperature at the deep site was only 1°C. The same trend is also shown in Table 1, by the high positive significant correlations between DOC and temperature when the data points were split into oxidized (with oxygen and nitrate) and reduced (no oxygen and nitrate). The shallow point had the highest flux of DOC out of the sediment in July when the temperature was at its peak (18°C). The shallow site DOC flux then decreased in autumn with negative fluxes in October and November. The sediment at the deep site became a source of DOC when the hypolimnion became anoxic in June. The DOC flux for the deep site remained positive in the autumn months and was of a similar magnitude throughout the stratification period.

To investigate whether there was an interconnection between the release of DOC and redox sensitive solutes we also measured the fluxes of other solutes (Fig. 3). Methane, SRP, Fe, and Mn were released at the deep site under anoxic conditions, in contrast there was uptake or negligible release at the shallow site. Sulfate uptake occurred at both, the deep and shallow site with the exception of April when both sites were oxic and November (shallow site only). Total inorganic carbon was released in both, the shallow and deep sites with the exception of April for deep site when a negative flux was recorded. Oxygen flux at the shallow site was negative indicating consumption (Fig. 3). The consumption trend was similar to the temperature trend, except that the maximum occurred later in September.

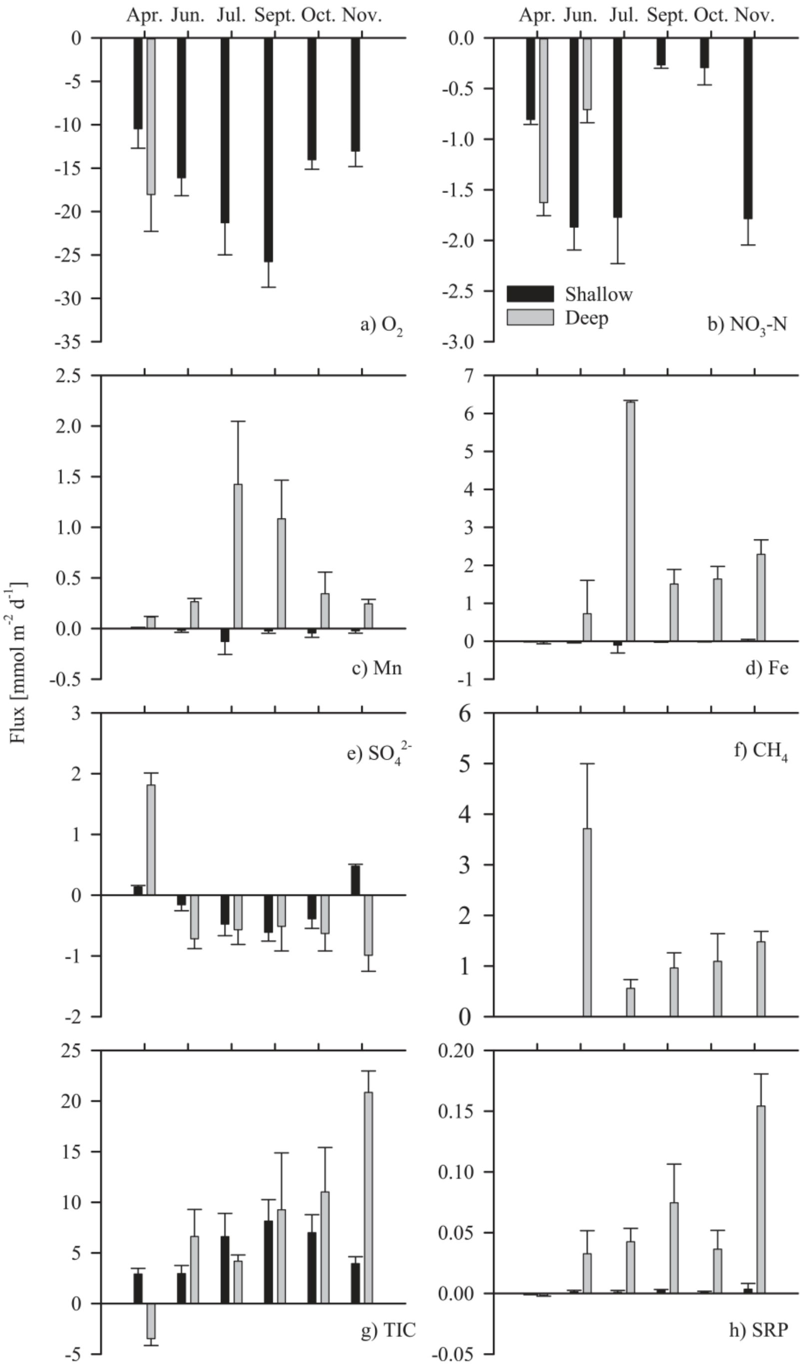

Fig. 3. Seasonal fluxes of O_2 (**a**), NO_3^- (**b**), Mn (**c**), Fe (**d**), SO_4^{2-} (**e**), CH_4 (**f**), TIC (**g**), and SRP (**h**) over time. Error bars represent standard deviation of four replicate cores.

A Pearson correlation analysis including all data revealed that the DOC flux was correlated with redox related parameters (Table 1): there was a significant negative correlation with concentrations of O_2, NO_3^-, and SO_4^{2-}, and a positive correlation with TIC concentration and flux, SRP concentration and Mn flux. Analyzing oxidized and reduced (no O_2 and no NO_3^-) situations separately revealed different correlations under oxidized and reduced conditions. In the presence of NO_3^- in the overlying water, the DOC flux was only correlated with temperature. In the absence of O_2 and NO_3^-, the DOC flux was negatively correlated with SO_4^{2-} flux and SRP concentration, and positively correlated with temperature. There were non-significant positive trends with Mn concentration, CH_4 flux, TIC flux, SRP flux, and NH_4^+, and a negative trend with the Mn flux. Directly after NO_3^- depletion there was an extraordinary high Fe flux out of the sediment (Fig. 3d deep site). Exclusion of this event from the analysis resulted in a high (0.99) significant ($p < 0.01$) correlation between DOC flux and Fe flux at the deep site. The plot of this data is shown in Fig. 2b. The DOC/Fe flux ratio was 1.5.

To assess the role of different anaerobic electron transport processes, we converted the fluxes of electron acceptors to electron fluxes (data not shown). At the shallow site, the

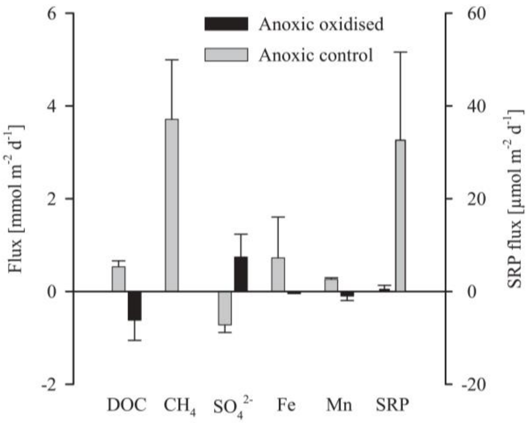

Fig. 4. Solute fluxes of deep site sediments incubated under different redox conditions at 4.2°C. The term "anoxic oxidized" refers to sediments sampled anoxic but oxidized prior to experiment while "anoxic control" refers to sediments sampled anoxic and incubated anoxic. Error bars show standard deviations from four replicate cores. Positive fluxes are directed from the sediment into the water. Dissolved organic carbon, CH_4, SO_4^{2-} and Mn were significantly different ($p < 0.05$) between the anoxic oxidized and anoxic control while there was no significant difference for Fe and SRP.

Table 2. Sediment properties and sedimentation at both sites. Water content and loss on ignition show annual mean and standard deviation $n = 24$.

	Shallow site	Deep site
Water content (% ww)*	84 ± 2	95 ± 1
Loss on ignition (% dw)*	14.8 ± 0.3	25 ± 0.3
Mean sedimentation (g m^{-2} yr^{-1})	3143 ± 1101*	627 ± 203†
C sedimentation (g m^{-2} yr^{-1})	295	83
Microbial biomass (μmol P g-dw^{-1})‡,§	1.0–1.4	3.0–3.6
HCl-soluble Fe(II) (μmol mL^{-1})‡,§	28–72	32–65
Hydroxylamine-reducible Fe(III) (μmol mL^{-1})‡,§	2–22	0–17
Fe(III) reducing prokaryotes (cells mL^{-1})‡,§	10^4–10^6	10^4–10^5

*$n = 4$.
†$n = 5$.
‡Weighted mean of the 0–1, 1–3, 3–5 cm sediment layers.
§Data are spring and summer ranges from Kloß (2013).

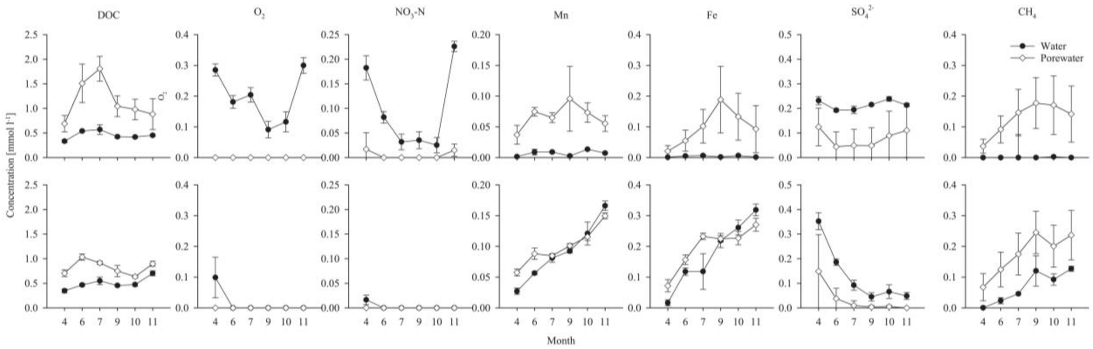

Fig. 5. Seasonal change of concentrations in the overlying water and in the porewater of the upper 5 cm (weighted mean of the 0–1, 1–3, 3–5 cm) at the shallow site (upper row) and the deep site (lower row).

Table 3. Benthic DOC fluxes in different aquatic systems. Values in brackets are DOC fluxes and temperatures under anoxic conditions.

System	Trophic state	Water depth (m)	DOC flux (mmol m^{-2} d^{-1})	Temp (°C)	References
Freshwater					
Hassel reservoir, Germany	Eutrophic	5*	−1.8 to 2.4 (0.5–2.5)	4–18 (4–6)	this study
Lake Apopka, Florida	Hypertrophic	4.7*	0.3	17–30	Gale and Reddy (1994)
Pond, China	Eutrophic	1.2*	−0.2	20–26	Zheng et al. (2011)
Uiam Lake, South Korea	Eutrophic	13.4*	4.8 (5.1)	20 (20)	Yang et al. (2014)
Quebec Lakes, Canada	Oligo-,meso-, eutrophic	1–26*	0–19.4	17–27	Demarty and Prairie (2009)
Sweet water reservoir, California	Oligo-/mesotrophic	9*	0.3–13.8	14–22	Downing et al. (2008)
Marine					
Long Island Sound, USA	Eutrophic	15†	−1.5 (5–127)	16 (16)	Skoog and Arias-Esquivel (2009)
Chesapeake Bay	Eutrophic	0–12†	1.4–2.9	6–26	Burdige and Homstead (1994)
San Diego Bay	Mesotrophic	7†	1.6	16–17	Chen et al. (1997)
Missionary Bay, Australia	Oligotrophic	0–1.3†	0	20	Boto et al. (1989)
Estuaries, Australia	Oligotrophic	0.5–2†	−9 to 41	17–26	Maher and Eyre (2010)

*Mean depth of lake.
†Sampling depth.

most important electron acceptors were O_2, NO_3^- and to a lesser extent SO_4^{2-} with Fe and Mn insignificant while methanogenesis was negligible. The deep site under oxic conditions (April) exhibited a similar trend as the shallow site. However, when the hypolimnion became anoxic during summer stratification, SO_4^{2-}, Fe, Mn, and CH_4 became relevant after nitrate depletion.

Oxygenation of anoxic sediments

To investigate the effect of oxygenation of anoxic sediments on the DOC flux, a parallel incubation experiment was carried out in June 2013. Anoxic sediment cores were sampled from the deep site and incubated under both oxic and anoxic conditions. The anoxic sediment was a source of DOC, SRP, Fe, Mn, and CH_4 and a sink for SO_4^{2-} (Fig. 4). Oxygenation either blocked fluxes nearly completely (CH_4, Fe, Mn, SRP) or even changed the direction of the flux (DOC, SO_4^{2-}). This response was consistent with the observed seasonal trends.

Resuspension experiments

Under oxic conditions resuspension indeed decreased the DOC concentration in the water (data not shown). One resuspension event removed -4.3 ± 3.2 mmol m^{-2} d^{-1} of DOC which is equivalent to 6 d of diffusive DOC consumption at 4°C. Under anoxic conditions, resuspension increased the concentration of both DOC and dissolved Fe in the water, showing that the oxidation step was necessary to strip DOC from the water.

Sediment porewater and carbon deposition

The DOC concentration in the sediment porewater was always higher than in the overlying water (Fig. 5). The concentration gradient between porewater and overlying water was rather constant at the deep site while, in agreement with higher DOC fluxes, it increased during summer at the shallow site. The porewater data at the shallow site followed a similar pattern to temperature, with the least DOC porewater concentration always in the 0–1 cm layer and the highest in the 3–5 cm and the 1–3 cm layer having a concentration in between. Similar to DOC, the concentration of Fe and Mn increased in the porewater during summer. Sulfate reduction as indicated by a negative concentration gradient was apparently active at both sites, but resulted in a depletion of SO_4^{2-} only at the deep site. Methane was produced in the sediment at both sites with apparently comparable rate, but accumulated in the overlying water only under anoxic conditions while it was completely oxidized under oxic conditions.

Availability of particulate organic carbon might be an important determinant of DOC production in the sediment. Sediment deposition at the shallow site was at least three times higher than at the deep site (Table 2). However, the carbon concentration of the sedimenting material was comparable between the two sites. The shallow site C sedimentation rate varied seasonally. It increased from spring and peaked in summer around 100 mmol C m^{-2} d^{-1}, while that at the deep site was constant around 20 mmol C m^{-2} d^{-1} throughout the year. The DOC flux correlated positively with C sedimentation rate, however, the correlation with organic matter content of the upper 5 cm was poor (Table 1).

Discussion

Direction and magnitude of the DOC flux

The DOC flux in this study is comparable both in direction and magnitude to previous studies summarized in Table 3. There are only a few studies on anoxic DOC fluxes and we find our values to be on the lower side from those reported by Skoog and Arias-Esquivel (2009) and Yang et al. (2014), which could be due to lower incubation temperatures of our experiments. Our data as well as that from the literature (Table 3) show that the sediment is always a DOC source under anoxic conditions, but can be a source or sink under oxic conditions. Apparently oxic conditions alone do not guarantee negative DOC fluxes, something which is critical for reservoir management. The apparent contradiction between elevated DOC concentrations in the sediment and at the same time a DOC flux from the water into the sediment in April, October, and November has also been observed in marine systems (Burdige and Homstead 1994) can be explained by DOC consumption at the sediment surface. Our vertical porewater resolution does not resolve small scale processes at the very sediment surface. However, our data clearly show the presence of a DOC consuming process which is bound to oxidized conditions.

Factors controlling benthic DOC flux

Our data reveal a two level control hierarchy of the regulatory mechanism: redox conditions and temperature. Both are closely connected as discussed later.

The first level is redox conditions. There are principal differences between oxidised and reduced conditions. Net consumption of DOC by the sediment seems to be only possible under oxic conditions and can be attributed to adsorption of DOC to mineral particles or enhanced biological consumption in the uppermost sediment (Burdige and Homstead 1994). The change from oxic to anoxic conditions resulted in DOC release, a trend also observed by Skoog and Arias-Esquivel (2009), in marine sediments. The DOC release could be interpreted in different ways; (1) reduction in DOC consumption possibly due to potential change in microbial activities as indicated by the dynamic nature of the relevance of electron acceptors, (2) increased DOC mobilization from redox sensitive minerals surfaces, which is further discussed in the next section below.

Redox conditions are generally discussed in the context of availability of oxygen, however, our data indicate that DOC flux was not only controlled by oxygen per se but also related to NO_3^- concentration. The highest DOC fluxes for the shallow site were in June and July when the NO_3^- concentration was the lowest. Nitrate keeps the redox potential high and prevents Fe reduction, which has been attributed to delay the release of redox sensitive solutes in other studies (Andersen 1982; Wauer et al. 2005). Furthermore, NO_3^- penetrates the sediment deeper than O_2 (Sweerts and De Beer 1989) resulting in a thicker oxidised sediment layer. The high Fe release in July following NO_3^- depletion (Fig. 3) was probably caused by initial dissolution of fresh Fe hydroxides at the sediment surface. This material contains probably less DOC and P than the “older” Fe-hydroxides in the sediment hence there was no corresponding peak in DOC (Fig. 2).

It has been shown that reducing conditions preserve organic matter because certain enzymes need molecular oxygen (Fenner and Freeman 2013). This would result in lower DOC degradation rates under anoxic conditions. Indeed it has been shown that reducing conditions did only slightly affect the degradation of “fresh” DOC, but slowed down the degradation of more recalcitrant DOC (Bastviken et al. 2004). Assuming no temperature effects and constant sediment C composition at the deep site, and no significant changes in microbial biomass between seasons (Kloß 2013), then the DOC flux was controlled by O_2 and NO_3^-. In April the sediment was oxic, giving a flux of -0.7 mmol m^{-2} d^{-1}. The mean DOC flux for the no O_2 and no NO_3^- period was 1.8 mmol m^{-2} d^{-1}. If we assume that a similar production of DOC proceeded in the anoxic sediment layers also in April, the total consumption in the oxic sediment layer in April was the sum of simultaneous DOC flux into the oxic sediment layer both from the water side but also from the anoxic sediment. Thus total DOC consumption in April was probably 2.5 mmol m^{-2} d^{-1}. The June situation (NO_3^- present, but no O_2) shows that NO_3^- probably reduced the extent of Fe reduction (Achtnich et al. 1995; Matocha and Coyne 2007), but was less potent as an oxidant compared with O_2 as shown in other studies (Kleeberg and Dudel 1997; Grüneberg et al. 2014). For an annual budget of the sediment at the deep site (see below) we assume a mean flux of -0.7 and 1.8 mmol m^{-2} d^{-1} under oxic vs. anoxic conditions.

The second level of regulation is temperature. DOC release under oxidized conditions was controlled by temperature as indicated by the positive correlation with temperature at both sites (Table 1). However, the temperature effect at the deep site has to be treated with caution because the annual variation in temperature at the deep site was about 1°C and the accuracy of our climate chambers where the incubations were done is ± 1°C. Temperature effects can be inferred from most freshwater DOC fluxes (Table 3) which shows that positive fluxes under oxic conditions occurred at temperature greater than 15°C in other studies.

Temperature may have a direct effect due to increased mineralization of particulate organic carbon to DOC by microbes in the sediments leading to increased DOC porewater concentration as shown by the trend of increasing oxygen consumption with increasing temperatures. The positive DOC flux during summer can be explained by temperature dependent increase in DOC production while DOC consumption in the surface sediment did not (or to a much lesser extent) change with temperature. A similar trend was observed by Alperin et al. (1994) in organic rich coastal sediment, which they attributed to temperature dependent particulate organic carbon hydrolysis between spring and autumn. By fitting a linear function to the DOC flux data above 9°C in Fig. 2a and subtracting the intercept (DOC consumption at 0°C) we calculated a temperature coefficient (Q_{10}) of 2.1 between 10° and 18°. This is typical for biological reactions, with Q_{10} in freshwaters ranging from 1.9 to 3.2 (Starink et al. 1996a; Liikanen et al. 2002). Identical Q_{10} values were calculated for the fluxes of Fe and SO_4^{2-} while the Q_{10} for O_2 consumption and TIC production were 1.6 and 1.5, respectively. This could be an indication that the DOC release processes during this time were strongly coupled to reduction of both SO_4^{2-} and Fe.

Our data suggests an indirect temperature control via temperature dependency of reduction of both SO_4^{2-} and Fe. Besides directly stimulating microbial Fe and SO_4^{2-} reduction, higher temperature also increased the O_2 consumption rate (Fig. 5) in the surface sediment thereby reducing the oxic sediment volume despite the oxic conditions in the overlying water. This will further stimulate Fe reduction and SO_4^{2-} reduction which produces hydrogen sulfide (H_2S). Hydrogen sulfide can influence accumulation of DOC in 2 ways: (1) inhibition of bacteria (Canfield 1994) thereby causing reduced turnover of DOC and (2) reduction and immobilization of Fe by the formation of FeS (Roden and Edmonds 1997) resulting in release of DOC adsorbed to ferric compounds. Increasing temperature has also been shown to decrease the adsorption of DOC to mineral surfaces (Arnarson and Keil 2000), which could have contributed to the positive DOC fluxes under high temperature conditions. A decrease in DOC adsorption implies increased availability to microbes.

Theoretically, the high DOC flux at the shallow site in summer could also be caused by the higher C sedimentation rate (Table 2). However this is based on the assumption that the settling particulate organic carbon is of a greater quality than what already existed in the sediment and will trigger higher mineralization of particulate organic carbon and subsequent accumulation of DOC as a by-product. We think, however, that the seasonal change of the DOC flux was caused by temperature rather than sedimentation because of the following reasons: there was a DOC porewater gradient from the anoxic sediment layers to the surface, showing that the site of DOC production was located in the anoxic sediment. The porewater concentration followed the same seasonal trend with higher concentrations in summer. Thus, there was always potential for a diffusive flux of DOC from deeper sediment layers toward the sediment surface. We assume that elevated DOC concentrations at 5 cm depth are not caused by freshly settled material but by higher temperatures in that sediment layer. Second, the carbon: nitrogen (C: N) ratio in settling material was constant throughout the year which indicates no change in organic substrate quality. Sedimentation would have an effect on DOC release if the quality of settling particulate organic matter is more labile than what is already in the sediment. If the quality remains the same then any increase in particulate organic matter mineralization to DOC is likely to be due to some other factors e.g., temperature in this case. Third, the sediment at the deep site contained much more organic carbon than the sediment at the shallow site and threefold microbial biomass compared with the shallow site (Table 2). If sedimentation was the driver of the DOC flux then the deep site should have had a higher DOC flux in April, when both the shallow and deep site were under oxic conditions.

Regulatory mechanism of benthic DOC flux

We hypothesized that the benthic DOC flux is regulated both by microbial production and interaction with Fe mineral surfaces. The previous section highlighted the temperature dependent microbial production and in this section we discuss the interaction with mineral surfaces. We suggest that sorption onto Fe oxides is probably the dominant process regulating the benthic DOC flux. The oxygenation of anoxic sediment experiment at the deep site (Fig. 4) in which the same sediment was incubated under different redox conditions clearly shows that release of DOC was accompanied by a non-significant Fe release trend under anoxic conditions while under oxic conditions the Fe flux show a non-significant trend toward Fe uptake by the sediments. Sorption to Fe minerals was further demonstrated by the resuspension experiment which under oxic conditions showed a decrease in DOC concentration after the resuspension, while under anoxic conditions there was an increase of DOC concentration in the overlying water. Microbial uptake (which should not be confused with microbial production) of DOC is also a potential regulatory mechanism proposed in other studies (Findlay et al. 1993; Fischer et al. 2002) because the sediment water interface is known to harbor diverse species of heterotrophic bacteria (Starink et al. 1996b; Christian and Lind 2007). With our results we can infer that either microbial uptake was not a major process under high temperature conditions or was limited by the quality of the DOC since there was neither a decline in DOC concentration nor a rapid increase in total inorganic carbon concentration in the overlying water under high temperature conditions as shown in other studies (Holmer 1996).

Adsorption of DOC to Fe minerals has been reported in many other studies (Jonsson 1997; Kaiser and Guggenberger 2000; Wagai and Mayer 2007; Lalonde et al. 2012). The porewater data show that DOC consumption was restricted to the sediment surface under oxic conditions while production of DOC proceeded in the anoxic sediment, even when the sediment surface was oxidized. Positive DOC fluxes were always accompanied by positive Fe fluxes (Fig. 2b) which fits well to the hypothesis that reductive dissolution of Fe hydroxides releases adsorbed DOC particles. Iron can be reduced either directly by Fe reducing microbes or indirectly by H_2S (Afonso and Stumm 1992), which has been produced by SO_4^{2-} reducing microbes. Most probable number counts proved the existence of Fe reducing bacteria in the sediment (Table 2) and both Fe(III) reduction and sulfate reduction have been detected at the deep site in different layers of the sediment (Wendt-Potthoff et al. 2014). The ongoing mineralization of organic matter by microbial Fe reduction and SO_4^{2-} reduction was also indicated by a decrease in SO_4^{2-} accompanied by increases in Fe(II), ammonium and TIC in the hypolimnion (Wendt-Potthoff et al. 2014). Regardless whether Fe is reduced directly or indirectly, it is a microbial process which depends on temperature. The adsorption of DOC to Fe hydroxides, conversely should be controlled by the availability of suitable mineral surfaces (Keil et al. 1994). Our OC: Fe ratio of 1.5 was at the lower end of literature values of 1–30 (Lalonde et al. 2012). Thus, Fe surfaces were probably not limiting DOC adsorption in our case. This is further supported by the higher water content of the sediment at the deeper site, indicating smaller particle size and higher particle surface area.

Implications for reservoir carbon cycling

Annually on average 84% of the Hassel pre-dam sediment surface was under oxic water while 16% was under anoxic water. In 2013 the highest surface area under anoxic water was 40% over a period of one month. Figure 6 show the seasonality of benthic DOC release from oxic and anoxic sediments, which translates to a benthic net DOC production of −344 and 165 kg yr^{-1} carbon under anoxic and oxic conditions respectively (Fig. 6). The sediments were therefore, a net sink of DOC (−178 kg yr^{-1}). In terms of the reservoirs carbon budget this is small compared with the DOC annual load of 15 tonnes (Friese et al. 2014). Thus, the quantitative importance of the benthic DOC flux in terms of the total carbon budget is small. It might be more relevant in lakes with higher residence time because they are dominated by autochthonous organic matter inputs (Groeger and Kimmel 1984) and also have higher organic matter mineralization (Den Heyer and Kalff 1998). From the results of our study we hypothesize that in shallow or nutrient poor lakes the sediment is probably a DOC sink, while in nutrient rich lakes it is rather a source of DOC.

Besides its low quantitative significance, adsorption to iron hydroxides can also affect DOC quality (Orem and Gaudette 1984; Riedel et al. 2013). It remains to be investigated whether Fe-DOC interactions at the sediment water interface modify the degradability of DOC in lakes. By summing up the fluxes of TIC, CH_4, and DOC we calculated the total carbon flux at the sediment water interface. The mean total carbon flux ($n = 6$) at the shallow site (5.4 ± 2.9 mmol m^{-2} d^{-1}) was half of that of the deep site (10.5 ± 8.7 mmol m^{-2} d^{-1}) which can be attributed to the difference in the organic matter content of the sediment. The DOC flux was in the magnitude of a tenth to a fifth of the total carbon flux, which makes it a significant process in the benthic carbon cycle. It was higher than long-term carbon accumulation rates in lake sediments which are typically between 1 mmol m^{-2} d^{-1} and 3 mmol m^{-2} d^{-1} (Tranvik et al. 2009) and thus, has an influence on long term storage of carbon on the continents (Cole et al. 2007).

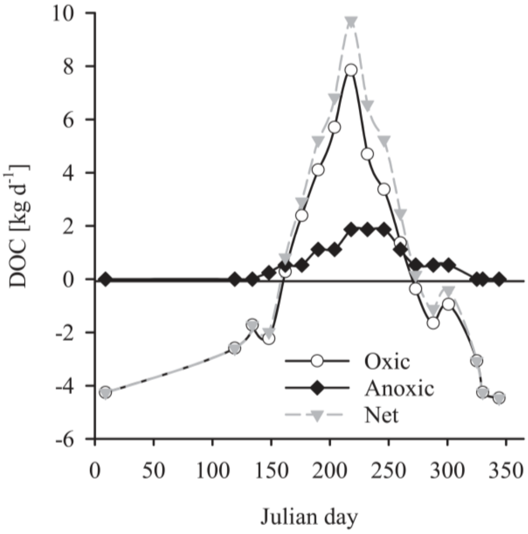

Fig. 6. Benthic DOC release from pre-dam sediment surfaces areas overlain by oxic and anoxic water. Net refers to the sum of the oxic and anoxic DOC release. Please note: the gap between the first 2 points represent the winter period when the pre-dam was covered with ice.

Global climate change results in higher surface water temperatures, which causes a higher productivity (Mooij et al. 2005) and stronger stratification (Wilhelm and Adrian 2008). Both effects favor anoxic conditions at the sediment water interface and thus potentially increase the benthic DOC flux. Theoretically, higher temperatures also stimulate microbial processes and thus both the reductive dissolution of ferric minerals and the degradation of organic matter. We consider this mechanism to be less relevant in lakes, because bottom water temperature is less affected by changing air temperatures. Although surely not the primary reason, DOC release from sediments has the potential to accelerate the observed temperature related increase of DOC in surface waters (Weyhenmeyer and Karlsson 2009). In reservoirs, the effects of warmer climate are probably more complex, because water level fluctuations are expected to increase in the future (Scharf 2013). One consequence of water level drawdown, which is usually accomplished by bottom water withdrawing, is a diminished area of anoxic sediment surfaces, which counteracts DOC increase.

Interestingly, the mechanism of benthic DOC dynamics as discussed in this article is very similar to the mechanisms governing benthic P dynamics and internal nutrient loading of lakes. We suppose that measures to reduce internal P loading of lakes, like deep water aeration or hypolimnetic water withdrawal might also be effective with regard to DOC.

References

Achtnich, C., F. Bak, and R. Conrad. 1995. Competition for electron donors among nitrate reducers, ferric iron reducers, sulfate reducers, and methanogens in anoxic paddy soil. Biol. Fertil. Soils **19**: 65–72. doi:10.1007/BF00336349

Afonso, M. D., and W. Stumm. 1992. Reductive dissolution of iron(III) (hydr)oxides by hydrogen sulfide. Langmuir **8**: 1671–1675. doi:10.1021/la00042a030

Alperin, M. J., D. B. Albert, and C. S. Martens. 1994. Seasonal variations in production and consumption rates of dissolved organic carbon in an organic-rich coastal sediment. Geochim. Cosmochim. Acta **58**: 4909–4930. doi:10.1016/0016-7037(94)90221-6

Alperin, M. J., and others. 1999. Benthic fluxes and porewater concentration profiles of dissolved organic carbon in sediments from the North Carolina continental slope. Geochim. Cosmochim. Acta **63**: 427–448. doi:10.1016/S0016-7037(99)00032-0

Andersen, J. M. 1982. Effect of nitrate concentration in lake water on phosphate release from the sediment. Water Res. **16**: 1119–1126. doi:10.1016/0043-1354(82)90128-2

Arnarson, T. S., and R. G. Keil. 2000. Mechanisms of pore water organic matter adsorption to montmorillonite. Mar. Chem. **71**: 309–320. doi:10.1016/S0304-4203(00)00059-1

Barber, A., K. Lalonde, A. Mucci, and Y. Gelinas. 2014. The role of iron in the diagenesis of organic carbon and nitrogen in sediments: A long-term incubation experiment. Mar. Chem. **162**: 1–9. doi:10.1016/j.marchem.2014.02.007

Bastviken, D., L. Persson, G. Odham, and L. Tranvik. 2004. Degradation of dissolved organic matter in oxic and anoxic lake water. Limnol. Oceanogr. **49**: 109–116. doi:10.4319/lo.2004.49.1.0109

Bergström, I., P. Kortelainen, J. Sarvala, and K. Salonen. 2010. Effects of temperature and sediment properties on benthic CO_2 production in an oligotrophic boreal lake. Freshw. Biol. **55**: 1747–1757. doi:10.1111/j.1365-2427.2010.02408.x

Biddanda, B. A., and J. B. Cotner. 2002. Love handles in aquatic ecosystems: The role of dissolved organic carbon drawdown, resuspended sediments, and terrigenous inputs in the carbon balance of Lake Michigan. Ecosystems **5**: 431–445. doi:10.1007/s10021-002-0163-z

Boto, K. G., D. M. Alongi, and A. L. J. Nott. 1989. Dissolved organic carbon-bacteria interactions at sediment-water interface in a tropical mangrove system. Mar. Ecol. Prog. Ser. **51**: 243–251. doi:10.3354/meps051243

Brothers, S., and others. 2014. A feedback loop links brownification and anoxia in a temperate, shallow lake. Limnol. Oceanogr. **59**: 1388–1398. doi:10.4319/lo.2014.59.4.1388

Burdige, D. J., M. J. Alperin, J. Homstead, and C. S. Martens. 1992. The role of benthic fluxes of dissolved organic carbon in oceanic and sedimentary carbon cycling. Geophys. Res. Lett. **19**: 1851–1854. doi:10.1029/92GL02159

Burdige, D. J., and J. Homstead. 1994. Fluxes of dissolved organic carbon from Chesapeake Bay sediments. Geochim. Cosmochim. Acta **58**: 3407–3424. doi:10.1016/0016-7037(94)90095-7

Canfield, D. E. 1994. Factors influencing organic-carbon preservation in marine-sediments. Chem. Geol. **114**: 315–329. doi:10.1016/0009-2541(94)90061-2

Chen, R. F., D. B. Chadwick, and S. H. Lieberman. 1997. The application of time-resolved spectrofluorometry to measuring benthic fluxes of organic compounds. Org. Geochem. **26**: 67–77. doi:10.1016/S0146-6380(96)00154-4

Christian, B. W., and O. T. Lind. 2007. Multiple carbon substrate utilization by bacteria at the sediment-water interface: Seasonal patterns in a stratified eutrophic reservoir. Hydrobiologia **586**: 43–56. doi:10.1007/s10750-006-0476-6

Cole, J. J., and others. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems **10**: 171–184. doi:10.1007/s10021-006-9013-8

Dadi, T., C. Völkner, and M. Koschorreck. 2015. A sediment core incubation method to measure the flux of dissolved organic carbon between sediment and water. J. Soils Sediments. doi:10.1007/s11368-015-1213-4

Davis, J. A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. Geochim. Cosmochim. Acta **46**: 2381–2393. doi:10.1016/0016-7037(82)90209-5

Demarty, M., and Y. T. Prairie. 2009. In situ dissolved organic carbon (DOC) release by submerged macrophyte-epiphyte communities in southern Quebec lakes. Can. J. Fish. Aquat. Sci. **66**: 1522–1531. doi:10.1139/F09-099

Den Heyer, C., and J. Kalff. 1998. Organic matter mineralization rates in sediments: A within- and among-lake study. Limnol. Oceanogr. **43**: 695–705. doi:10.4319/lo.1998.43.4.0695

Downing, B. D., B. A. Bergamaschi, D. G. Evans, and E. Boss. 2008. Assessing contribution of DOC from sediments to a drinking-water reservoir using optical profiling. Lake Reserv. Manag. **24**: 381–391. doi:10.1080/07438140809354848

Fenner, N., and C. Freeman. 2013. Carbon preservation in humic lakes; a hierarchical regulatory pathway. Glob. Change Biol. **19**: 775–784. doi:10.1111/gcb.12066

Findlay, S., D. Strayer, C. Goumbala, and K. Gould. 1993. Metabolism of streamwater dissolved organic carbon in the shallow hyporheic zone. Limnol. Oceanogr. **38**: 1493–1499. doi:10.4319/lo.1993.38.7.1493

Fischer, H., A. Sachse, C. E. W. Steinberg, and M. Pusch. 2002. Differential retention and utilization of dissolved organic carbon by bacteria in river sediments. Limnol. Oceanogr. **47**: 1702–1711. doi:10.4319/lo.2002.47.6.1702

Freeman, C., C. D. Evans, D. T. Monteith, B. Reynolds, and N. Fenner. 2001a. Export of organic carbon from peat soils. Nature **412**: 785–785. doi:10.1038/35090628

Freeman, C., N. Ostle, and H. Kang. 2001b. An enzymic 'latch' on a global carbon store. Nature **409**: 149. doi: 10.1038/35051650

Friese, K., and others. 2014. Ecological response of two hydro-morphological similar pre-dams to contrasting land-use in the Rappbode reservoir system (Germany). Int. Rev. Hydrobiol. **99**: 335–349. doi:10.1002/iroh.201301672

Galapate, R. P., A. U. Baes, and M. Okada. 2001. Transformation of dissolved organic matter during ozonation: Effects on trihalomethane formation potential. Water Res. **35**: 2201–2206. doi:10.1016/S0043-1354(00)00489-9

Gale, P. M., and K. R. Reddy. 1994. Carbon flux between sediment and water column of a shallow, subtropical, hypereutrophic lake. J. Environ. Qual. **23**: 965–972. doi: 10.2134/jeq1994.00472425002300050017x

Gough, R., P. J. Holliman, N. Willis, and C. Freeman. 2014. Dissolved organic carbon and trihalomethane precursor removal at a UK upland water treatment works. Sci. Total Environ. **468**: 228–239. doi:10.1016/j.scitotenv.2013.08.048

Groeger, A. W., and B. L. Kimmel. 1984. Organic matter supply and processing in lakes and reservoirs. Lake Reserv. Manag. **1**: 282–285. doi:10.1080/07438148409354525

Grüneberg, B., T. Dadi, C. Lindim, and H. Fischer. 2014. Effects of nitrogen and phosphorus load reduction on benthic phosphorus release in a riverine lake. Biogeochemistry **123**: 185–202. doi:10.1007/s10533-014-0062-3

Gudasz, C., D. Bastviken, K. Steger, K. Premke, S. Sobek, and L. J. Tranvik. 2010. Temperature-controlled organic carbon mineralization in lake sediments. Nature **466**: 478–481. doi:10.1038/nature09186

Gudasz, C., D. Bastviken, K. Premke, K. Steger, and L. J. Tranvik. 2012. Constrained microbial processing of allochthonous organic carbon in boreal lake sediments. Limnol. Oceanogr. **57**: 163–175. doi:10.4319/lo.2012.57.1.0163

Guillemette, F., and P. A. Del Giorgio. 2012. Simultaneous consumption and production of fluorescent dissolved organic matter by lake bacterioplankton. Environ. Microbiol. **14**: 1432–1443. doi:10.1111/j.1462-2920.2012.02728.x

Hansen, L. S., and T. H. Blackburn. 1991. Aerobic and anaerobic mineralization of organic material in marine sediment microcosms. Mar. Ecol. Prog. Ser. **75**: 283–291. https://apps.webofknowledge.com/full_record.do?product=UA&search_mode=GeneralSearch&qid=8&SID=Z1FLp8xcw3Bp9U9bR51&page=1&doc=1

Holmer, M. 1996. Composition and fate of dissolved organic carbon derived from phytoplankton detritus in coastal marine sediments. Mar. Ecol. Prog. Ser. **141**: 217–228. doi:10.3354/meps141217

Hupfer, M., and J. Lewandowski. 2008. Oxygen controls the phosphorus release from lake sediments—a long-lasting paradigm in limnology. Int. Rev. Hydrobiol. **93**: 415–432. doi:10.1002/iroh.200711054

Jones, R. I., P. J. Shaw, and H. De Haan. 1993. Effects of dissolved humic substances on the speciation of iron and phosphate at different pH and ionic strength. Environ. Sci. Technol. **27**: 1052–1059. doi:10.1021/es00043a003

Jonsson, A. 1997. Fe and Al sedimentation and their importance as carriers for P, N and C in a large humic lake in northern Sweden, p. 283–295. *In* R. D. Evans, J. Wisniewski and J. Wisniewski [eds.], The interactions between sediments and water. Springer Netherlands.

Kaiser, K., and G. Guggenberger. 2000. The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. Org. Geochem. **31**: 711–725. doi:10.1016/s0146-6380(00)00046-2

Keil, R. G., D. B. Montlucon, F. G. Prahl, and J. I. Hedges. 1994. Sorptive preservation of labile organic matter in marine sediments. Nature **370**: 549–552. doi:10.1038/370549a0

Kleeberg, A., and G. E. Dudel. 1997. Changes in extent of phosphorus release in a shallow lake (Lake Grosser Muggelsee; Germany, Berlin) due to climatic factors and load. Mar. Geol. **139**: 61–75. doi:10.1016/S0025-3227(96)00099-0

Kloß, C. 2013. Mikrobiologisch-biogeochemische Charakterisierung von Sedimenten aus Trinkwassertalsperren (Microbiological and biogeochemical characterization of sediments from drinking water reservoirs). Master thesis. Magdeburg-Stendal Univ. of Applied Sciences.

Koelmans, A. A., and L. Prevo. 2003. Production of dissolved organic carbon in aquatic sediment suspensions. Water Res. **37**: 2217–2222. doi:10.1016/S0043-1354(02)00581-X

Kortelainen, P. 1993. Content of total organic-carbon in Finnish lakes and its relationship to catchment characteristics. Can. J. Fish. Aquat. Sci. **50**: 1477–1483. doi:10.1139/f93-168

Lalonde, K., A. Mucci, A. Ouellet, and Y. Gelinas. 2012. Preservation of organic matter in sediments promoted by iron. Nature **483**: 198–200. doi:10.1038/nature10855

Laskov, C., C. Herzog, J. Lewandowski, and M. Hupfer. 2007. Miniaturized photometrical methods for the rapid analysis of phosphate, ammonium, ferrous iron, and sulfate in pore water of freshwater sediments. Limnol. Oceanogr.: Methods **5**: 63–71. doi:10.4319/lom.2007.5.63

Liikanen, A., T. Murtoniemi, H. Tanskanen, T. Väisänen, and P. J. Martikainen. 2002. Effects of temperature and oxygen availability on greenhouse gas and nutrient dynamics in sediment of a eutrophic Mid-Boreal lake. Biogeochemistry **59**: 269–286. doi:10.2307/1469786

Luider, C., E. Petticrew, and P. J. Curtis. 2003. Scavenging of dissolved organic matter (DOM) by amorphous iron hydroxide particles $Fe(OH)_{3(S)}$, p. 37–41. *In* B. Kronvang [ed.], The interactions between sediments and water. Developments in Hydrobiology. Springer Netherlands.

Maher, D. T., and B. D. Eyre. 2010. Benthic fluxes of dissolved organic carbon in three temperate Australian estuaries: Implications for global estimates of benthic DOC fluxes. J. Geophys. Res. **115**. G04039, doi:10.1029/2010JG001433

Maloney, K. O., D. P. Morris, C. O. Moses, and C. L. Osburn. 2005. The role of iron and dissolved organic carbon in the absorption of ultraviolet radiation in humic lake water. Biogeochemistry **75**: 393–407. doi:10.1007/s10533-005-1675-3

Maranger, R., and M. J. Pullin. 2003. Elemental complexation by dissolved organic matter in lakes: Implications for Fe speciation and the speciation and the bioavailability of Fe and P, p. 185–214. *In* S.E.G.F.L. Sinsabaugh [ed.], Aquatic Ecosystems. Academic Press.

Matocha, C. J., and M. S. Coyne. 2007. Short-term response of soil iron to nitrate addition. Soil Sci. Soc. Am. J. **71**: 108–117. doi:10.2136/sssaj2005.0170

Matthews, D. A., S. W. Effler, C. T. Driscoll, S. M. O'donnell, and C. M. Matthews. 2008. Electron budgets for the hypolimnion of a recovering urban lake, 1989–2004: Response to changes in organic carbon deposition and availability of electron acceptors. Limnol. Oceanogr. **53**: 743–759. doi:10.4319/lo.2008.53.2.0743

Monteith, D. T., and others. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature **450**: 537–540. doi:10.1038/nature06316

Mooij, W. M., and others. 2005. The impact of climate change on lakes in the Netherlands: A review. Aquat. Ecol. **39**: 381–400. doi:10.1007/s10452-005-9008-0

Mortimer, C. H. 1942. The exchange of dissolved substances between mud and water in lakes. J. Ecol. **30**: 147–201. doi:10.2307/2256691

Orem, W. H., and H. E. Gaudette. 1984. Organic matter in anoxic marine pore water: Oxidation effects. Org. Geochem. **5**: 175–181. doi:10.1016/0146-6380(84)90003-2

Peura, S., H. Nykanen, P. Kankaala, A. Eiler, M. Tiirola, and R. I. Jones. 2014. Enhanced greenhouse gas emissions and changes in plankton communities following an experimental increase in organic carbon loading to a humic lake. Biogeochemistry **118**: 177–194. doi:10.1007/s10533-013-9917-2

Riedel, T., D. Zak, H. Biester, and T. Dittmar. 2013. Iron traps terrestrially derived dissolved organic matter at redox interfaces. Proc. Natl. Acad. Sci. USA **110**: 10101–10105. doi:10.1073/pnas.1221487110

Rinke, K., and others. 2013. Reservoirs as sentinels of catchments: The Rappbode Reservoir Observatory (Harz Mountains, Germany). Environ. Earth Sci. **69**: 523–536. doi:10.1007/s12665-013-2464-2

Roden, E. E., and J. W. Edmonds. 1997. Phosphate mobilization in iron-rich anaerobic sediments: Microbial Fe(III) oxide reduction versus iron-sulfide formation. Arch. Hydrobiol. **139**: 347–378. http://cat.inist.fr/?aModele=afficheN&cpsidt=2779163

Rodriguez, P., J. Ask, C. L. Hein, M. Jansson, and J. Karlsson. 2013. Benthic organic carbon release stimulates bacterioplankton production in a clear-water subarctic lake. Freshw. Sci. **32**: 176–182. doi:10.1899/12-005.1

Sachse, A., D. Babenzien, G. Ginzel, J. Gelbrecht, and C. E. W. Steinberg. 2001. Characterization of dissolved organic carbon (DOC) in a dystrophic lake and an adjacent fen. Biogeochemistry **54**: 279–296. doi:10.1023/A:1010649227510

Scharf, W. 2013. Climate change and water quality in deep-stratifying reservoirs—what would happen otherwise? Korrespondenz Wasserwirtschaft **6**: 248–254. doi:10.3243/kwe2013.05.001

Skoog, A., P. O. J. Hall, S. Hulth, N. Paxeus, M. R. Vanderloeff, and S. Westerlund. 1996. Early diagenetic production and sediment-water exchange of fluorescent dissolved organic matter in the coastal environment. Geochim. Cosmochim. Acta **60**: 3619–3629. doi:10.1016/0016-7037(96)83275-3

Skoog, A. C., and V. A. Arias-Esquivel. 2009. The effect of induced anoxia and reoxygenation on benthic fluxes of organic carbon, phosphate, iron, and manganese. Sci. Total Environ. **407**: 6085–6092. doi:10.1016/j.scitotenv.2009.08.030

Starink, M., M.-J. Bär-Gilissen, R. P. M. Bak, and T. E. Cappenberg. 1996a. Bacterivory by heterotrophic nanoflagellates and bacterial production in sediments of a freshwater littoral system. Limnol. Oceanogr. **41**: 62–69. doi:10.4319/lo.1996.41.1.0062

Starink, M., M.-J. Bär-Gilissen, R. P. M. Bak, and T. E. Cappenberg. 1996b. Seasonal and spatial variations in heterotrophic nanoflagellate and bacteria abundances in sediments of a freshwater littoral zone. Limnol. Oceanogr. **41**: 234–242. doi:10.4319/lo.1996.41.2.0234

Steinberg, C. E. W., and others. 2006. Dissolved humic substances—ecological driving forces from the individual to the ecosystem level? Freshw. Biol. **51**: 1189–1210. doi:10.1111/j.1365-2427.2006.01571.x

Sweerts, J.-P.R.A., and D. De Beer. 1989. Microelectrode measurements of nitrate gradients in the littoral and profundal sediments of a meso-eutrophic lake (Lake Vechten, The Netherlands). Appl. Environ. Microbiol. **55**: 754–757. http://www.ncbi.nlm.nih.gov/pmc/articles/PMC184192/

Taillefert, M., V. C. Hover, T. F. Rozan, S. M. Theberge, and G. W. Luther. 2002. The influence of sulfides on soluble organic-Fe(III) in anoxic sediment porewaters. Estuaries **25**: 1088–1096. doi:10.1007/BF02692206

Tipping, E. 1981. The adsorption of aquatic humic substances by iron oxides. Geochim. Cosmochim. Acta **45**: 191–199. doi:10.1016/0016-7037(81)90162-9

Tipping, E., and C. Woof. 1983. Elevated concentrations of humic substances in a seasonally anoxic hypolimnion:

Evidence for co-accumulation with iron. Arch. Hydrobiol. **98**: 137–145. https://apps.webofknowledge.com/full_record.do?product=UA&search_mode=GeneralSearch&qid=6&SID=Z1FLp8xcw3Bp9U9bR51&page=1&doc=1

Tranvik, L. J., and others. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr. **54**: 2298–2314. doi:10.4319/lo.2009.54.6_part_2.2298

Van Den Meersche, K., J. J. Middelburg, K. Soetaert, P. Van Rijswijk, H. T. S. Boschker, and C. H. R. Heip. 2004. Carbon-nitrogen coupling and algal-bacterial interactions during an experimental bloom: Modeling a ^{13}C tracer experiment. Limnol. Oceanogr. **49**: 862–878. doi:10.4319/lo.2004.49.3.0862

Wagai, R., and L. M. Mayer. 2007. Sorptive stabilization of organic matter in soils by hydrous iron oxides. Geochim. Cosmochim. Acta **71**: 25–35. doi:10.1016/j.gca.2006.08.047

Wauer, G., T. Gonsiorczyk, K. Kretschmer, P. Casper, and R. Koschel. 2005. Sediment treatment with a nitrate-storing compound to reduce phosphorus release. Water Res. **39**: 494–500. doi:10.1016/j.watres.2004.10.017

Wendt-Potthoff, K., C. Kloß, M. Schultze, and M. Koschorreck. 2014. Anaerobic metabolism of two hydromorphological similar pre-dams under contrasting nutrient loading (Rappbode Reservoir System, Germany). Int. Rev. Hydrobiol. **99**: 350–362. doi:10.1002/iroh.201301673

Weyhenmeyer, G. A., and J. Karlsson. 2009. Nonlinear response of dissolved organic carbon concentrations in boreal lakes to increasing temperatures. Limnol. Oceanogr. **54**: 2513–2519. doi:10.4319/lo.2009.54.6_part_2.2513

Wilhelm, S., and R. Adrian. 2008. Impact of summer warming on the thermal characteristics of a polymictic lake and consequences for oxygen, nutrients and phytoplankton. Freshw. Biol. **53**: 226–237. doi:10.1111/j.1365-2427.2007.01887.x

Yang, L., J. H. Choi, and J. Hur. 2014. Benthic flux of dissolved organic matter from lake sediment at different redox conditions and the possible effects of biogeochemical processes. Water Res. **61**: 97–107. doi:10.1016/j.watres.2014.05.009

Zheng, Z., J. Lv, K. Lu, C. Jin, J. Zhu, and X. Liu. 2011. The impact of snail (*Bellamya aeruginosa*) bioturbation on sediment characteristics and organic carbon fluxes in an eutrophic pond. Clean Soil Air Water **39**: 566–571. doi:10.1002/clen.201000212

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Chapter 4b: Benthic dissolved organic carbon fluxes in three drinking water reservoirs

Photo: A stream with heavily coloured brown water after a rain event. Muldenberg, September 2014. Photo by Tallent Dadi

4.1 Overview

Chapter 4a presented the organic carbon fluxes in Hassel pre-dam and this work is published in Dadi et al. (2016). Similar work was carried out in Rappbode and Rote Mulde however this work is not yet published. In this chapter I present results of all 3 pre-dams, focusing on comparisons. This was done to check whether the results obtained from Hassel pre-dam can be generalized. Hassel and Rappbode pre-dams have similar DOC mobilization/immobilization trend under both oxic and anoxic conditions. Rote Mulde has a similar DOC mobilization/immobilization trend to that of the shallow sites in Hassel and Rappbode; however the flux magnitude was distinctly higher. The fluxes of other solutes were generally higher in Hassel than Rappbode with the exception of TIC, while in Rote Mulde they were relatively lower than those of Hassel and Rappbode.

4.2 Abstract

Benthic DOC exchange in the three pre-dams was compared to determine similarities and differences. In all pre-dams, generally DOC was immobilized under oxic conditions and mobilized under anoxic conditions. However there were differences in magnitude, with Rote Mulde having a higher immobilization effect compared to Hassel and Rappbode. Immobilization of DOC in Rappbode under anoxic conditions was higher than in Hassel. The benthic DOC flux in Hassel and Rappbode is temperature dependent at the shallow sites; however in Rote Mulde this trend was very weak. Pooled data from all pre-dams showed a positive correlation between DOC and Fe under anoxic conditions at the deep sites, and a negative correlation under oxic conditions at the shallow sites. Carbon burial rates in Hassel are higher compared to those of Rappbode and Rote Mulde, which are similar. This could be due to the eutrophic state of Hassel. Pre-dam differences in catchment land use, trophic state, DOC concentration seem not to influence DOC mobilization/immobilization trends but rather the magnitude.

4.3 Introduction

The three pre-dams investigated share similarities and also have striking differences. Rote Mulde is much more different from the Hassel and Rappbode by being: smaller, having higher DOC concentration, lower pH and having a predominantly forested catchment. Hassel and Rappbode are very similar in terms of size, morphometry, and pH, however Hassel is eutrophic and Rappbode is oligotrophic just like Rote Mulde. Friese et al. (2014) found the concentration of major ions to be higher in Hassel than Rappbode as a result of the agricultural activities in the catchment of the former. The effect of benthic processes on the pre-dam system depends on surface area depth ratio. Benthic processes of systems with a lower surface area depth ratio (in this case Rote Mulde) have more effect than systems with a higher surface area depth ratio (in this case Hassel and Rappbode).

Water residence time is also a crucial aspect; apparently Rote Mulde has shorter water residence time compared to Hassel and Rappbode (Chapter 2, Table 2.1). Lakes with a high water residence time have higher nutrient retention (Kõiv et al. 2011), higher sedimentation, and are more influenced by internal bacteria (Lindstrom et al. 2005), in comparison to lakes with short water residence time .Water pH plays a role in mobilization/immobilization of DOC since it has an effect on surface charge and ionic strength, hence pH can alter adsorption properties of DOC (Tipping 1981; Gu et al. 1994). Leaching of DOC has been observed in other studies (Andersson et al. 1994; Evans et al. 2012). Therefore Rote Mulde can be expected to have a higher DOC immobilization potential. The objective of this chapter is to compare DOC benthic flux from the 3 pre-dams taking into account similarities and differences in characteristics of the pre-dams.

4.4 Methods

This section only provides an overview of the sampling campaigns and parameters analysed for each pre-dam. The procedures have already been described in Chapter 4a. Hassel was sampled in April, June, July, September, October, and November 2013. Rappbode was sampled in March, April, June, July, September, and October 2014. Rote Mulde was sampled in April, June and September in both 2013 and 2014. For Hassel all the parameters (DOC, $UV_{254\,nm}$ TIC, CH_4, NH_4^+, NO_3^- , SRP, SO_4^{2-} , Fe, and Mn) were measured for all campaigns in cores, controls, and porewater, with the exception of NH_4^+ only in porewater. For Rappbode all the parameters were only analysed in March, June, and September; in April, July, and October, only DOC, $UV_{254\ nm}$ TIC, and CH_4 were analysed. In Rote Mulde all parameters were analysed for all campaigns in 2013, while in 2014 only DOC, UV_{254nm} TIC and CH_4 were analysed. The sediment core sampling, laboratory sampling and analysis procedure in Rappbode and Rote Mulde is the same as the one used in Hassel (Chapter 4a.).

4.5 Results

4.5.1 Background properties

Benthic carbon dynamics are influenced by sedimentation and sediment quality, an overview of which is presented in Table 4.1. The deep site in Hassel and Rappbode had a higher water content compared to the shallow sites. Rote Mulde water content was similar to the shallow site however it was relatively higher. Loss on ignition which is a proxy for organic matter content showed that Rote Mulde had the highest organic matter content with the shallow sites having the least organic matter content. Mean annual sedimentation was highest at the shallow sites of Hassel and Rappbode and least in Rote Mulde. Carbon sedimentation also followed a similar trend like sedimentation however it was similar for deep sites and Rote Mulde.

Bottom water solutes concentrations at the time of sampling (Table 4.1) showed similarities between shallow sites in Hassel and Rappbode, with the exception of nitrate, which was relatively higher in Hassel than in Rappbode. Likewise the Hassel and Rappbode deep site also had similar solutes concentrations, with the exception of ammonium, which was relatively higher in Hassel than in Rappbode. There was a remarkable solutes concentrations difference between the shallow and deeps sites in Hassel and Rappbode. Rote Mulde solutes concentrations are comparable to the shallow sites of Hassel and Rappbode; however it had a higher DOC concentration than at the Hassel and Rappbode, and a relatively higher iron concentration as well.

4.5.2 Benthic DOC and other solutes fluxes

Hassel and Rappbode pre-dams had very similar DOC flux trends (Fig. 4.1.). Anoxia resulted in release of DOC in both pre-dams. Interestingly, a similar trend was observed when Rappbode shallow site was anoxic in July. Oxic conditions resulted in both immobilization and mobilization of DOC, a trend which seem to have been influenced by temperature which in this study is related to the season. Rote Mulde exhibited a stronger immobilization of DOC compared to the shallow sites of Hassel and Rappbode. However there was an exceptionally high mobilization of DOC in Rote Mulde in July 2013 albeit under oxic conditions. Rote Mulde also did not show a strong temperature dependency of the DOC flux.

Other solutes were analysed to elucidate the major drivers and mechanisms regulating DOC flux in the pre-dams. Rote Mulde had lower fluxes for other solutes compared to Hassel and Rappbode (Fig. 4.2). Nitrate consumption occurred in all pre-dams regardless of the redox conditions, however from July to November the deep sites had no nitrate at the time of sampling. Release of Fe and Mn occurred under anoxic conditions in Hassel and Rappbode, with the fluxes being higher in Hassel. The Fe, Mn and SRP fluxes showed a similar flux direction to that of DOC (Fig. 4.1 and 4.2). Sulphate was mainly consumed by the sediment, however sulphate production was also observed. Methane was only produced under anoxic conditions, while TIC was produced under both anoxic and oxic conditions, with TIC consumption only observed on one occasion in Hassel and Rote Mulde. Generally the fluxes of all the other solutes were of a higher magnitude in Hassel, than Rappbode, with the exception of TIC.

Table 4.1: Sediment characteristics, sedimentation rates, and bottom water chemical quality at the time of sampling, of the three pre-dams. [a] n = 4, [b] n = 5, [c] n = 7, [d] n = 6. Water content and loss on ignition show annual mean and standard deviation n = 24 for all pre-dams

	Hassel		**Rappbode**		**Rote Mulde**
	shallow	**deep**	**shallow**	**deep**	**2013 & 2014**
Water content [% ww]	84 ± 2	95 ± 1	63 ± 9	91 ± 2	84.5 ± 9.7
Loss on ignition [% dw]	14.8 ± 0.3	25 ± 0.3	9.4 ± 1.7	19.2 ± 0.6	29.5 ± 8.2
Sedimentation [g m^{-2} y^{-1}]	3143 ± 1101[a]	627 ± 203[b]	1825 ± 1211[b]	537 ± 244[c]	356 ± 131[d]
C sedimentation [g m^{-2} y^{-1}]	295 ± 132	83 ± 19	263 ± 126	88 ± 35	80 ± 28
DOC [mmol l^{-1}]	0.4 - 0.6	0.3 - 0.6	0.2 - 0.5	0.2 - 0.5	0.4 - 1.9
TIC [mmol l^{-1}]	0.4 - 1.0	0.8 - 2.3	0.6 - 1.2	0.5 - 1.6	0.1 - 0.6
NO_3^- [µmol l^{-1}]	50 - 300	3 - 160	16 - 61	3 - 60	6 - 50
NH_4^+ [µmol l^{-1}]	2 - 8	50 - 220	2 - 8	2 - 110	1 - 4
SO_4^{2-} [mmol l^{-1}]	0.2 - 0.3	0.1 - 0.2	0.2 - 0.3	0.1 - 0.2	0.1-0.2
SRP [µmol l^{-1}]	0 - 0.1	0 - 4	0-0.1	0 - 0.1	0 - 0.03
Mn [µmol l^{-1}]	0 - 1	8 - 126	2 - 14	2 - 100	5 - 11
Fe [µmol l^{-1}]	1 - 12	1 - 130	3 - 9	1 - 150	6 - 16

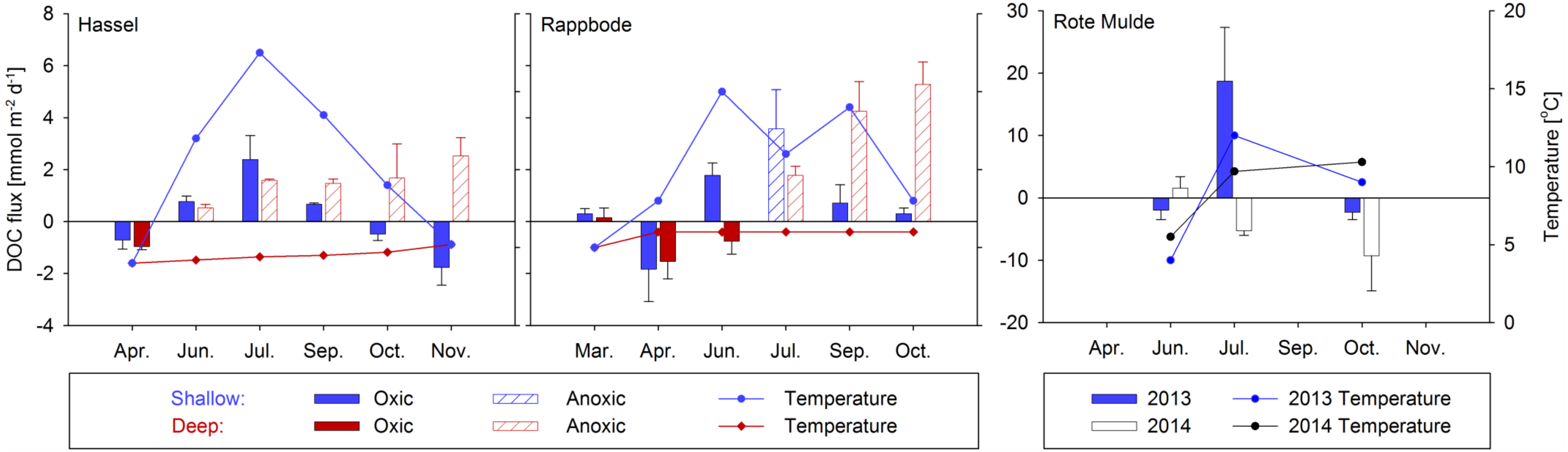

Fig. 4.1. Seasonal DOC flux and temperature for the 3 pre-dams. Error bars represent standard deviation of four replicates cores. Please note the Rote Mulde has a different DOC scale.

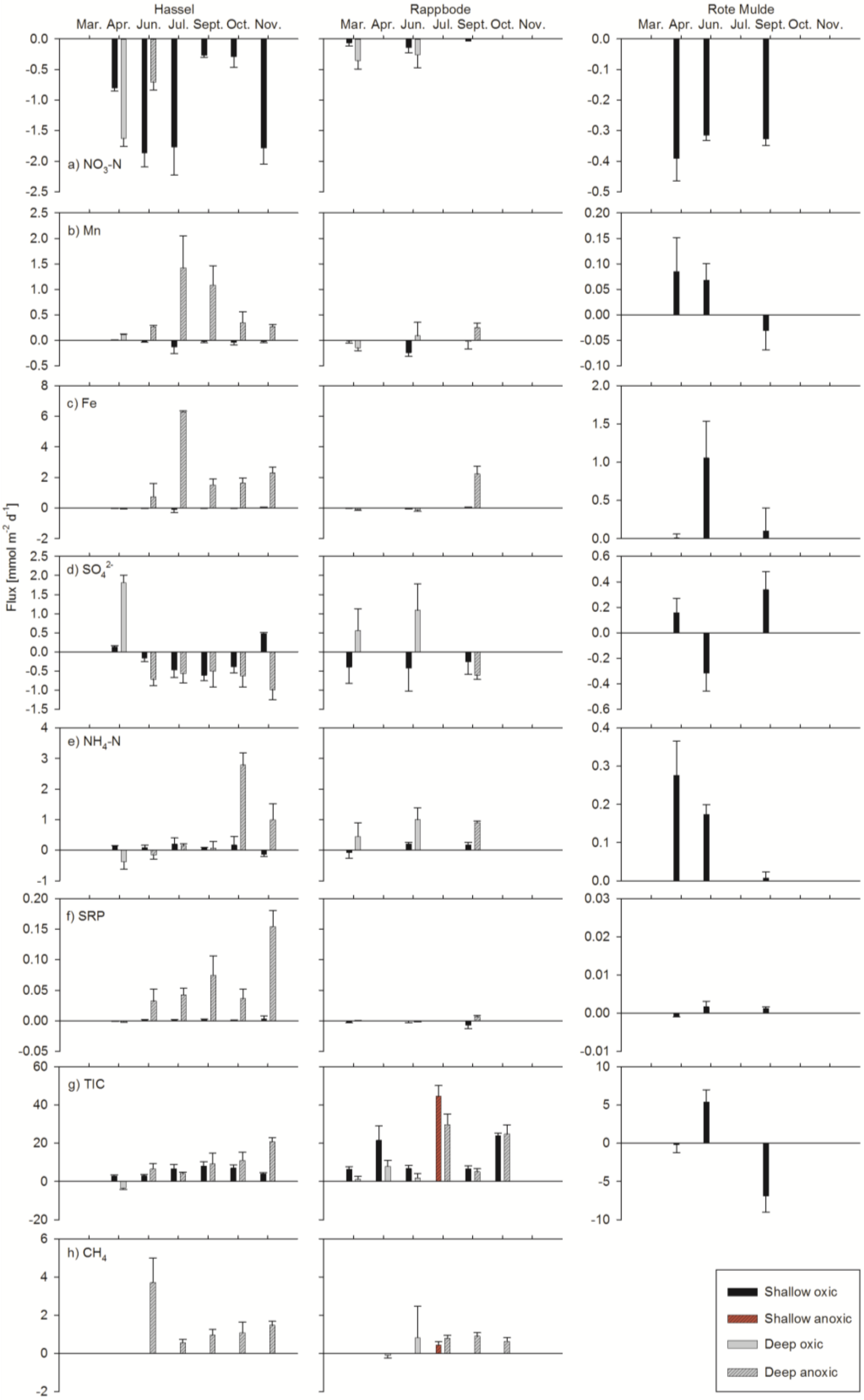

Fig. 4.2: Benthic fluxes of other solutes; (a) NO_3^- (b), Mn, (c) Fe, (d) SO_4^{2-} , (e) NH_4^+, (f) SRP, (g) TIC, and (h) CH_4, for the three pre-dams. Error bars represent standard deviation of 4 replicate cores. Please note the Hassel and Rappbode have one scale and Rote Mulde has a different scale, there was no CH_4 in the shallow sites including Rote Mulde, and for Rote Mulde the data shown is from 2013.

In Fig. 4.1 there was an indication that DOC fluxes were temperature dependent. All oxic DOC fluxes for shallow sites in Hassel and Rappbode, and all the fluxes from Rote Mulde were plotted. Fig. 4.3a shows this DOC flux/temperature plot for all the 3 pre-dams and it shows a weak positive correlation. As highlighted before, Rote Mulde seems to have a weaker DOC flux temperature dependency, so the data was removed from the plots. The resulting Fig. 4.3b shows a strong positive correlation of DOC flux and temperature. Removal of the data from Rappbode (as shown in Dadi et al. (2016), Chapter 4a, Fig. 2b) shows that the DOC flux temperature dependency was strongest in the Hassel pre-dam.

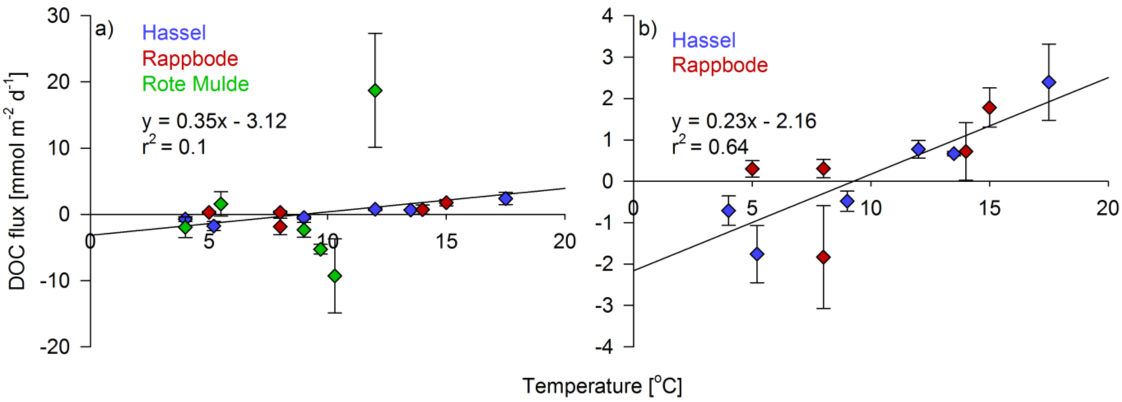

Fig. 4.3. DOC flux and temperature relationship at the shallow sites under oxic conditions; a) all 3 pre-dams, and b) only Hassel and Rappbode data. Error bars represent standard deviation of four replicates cores. Please note (b) has a different scale.

Oxygen consumption also correlated with positively with temperature and DOC flux (Fig. 4.4). In Hassel there was a strong positive correlation between DOC and Fe fluxes (Chapter 4a). Thus, it was checked whether the same holds true also for the other pre-dams. Figure 4.4a shows a strong positive correlation of DOC and Fe fluxes under anoxic conditions. In contrast under oxic conditions there was a strong negative correlation between DOC and Fe fluxes (Fig. 4.5b, c).

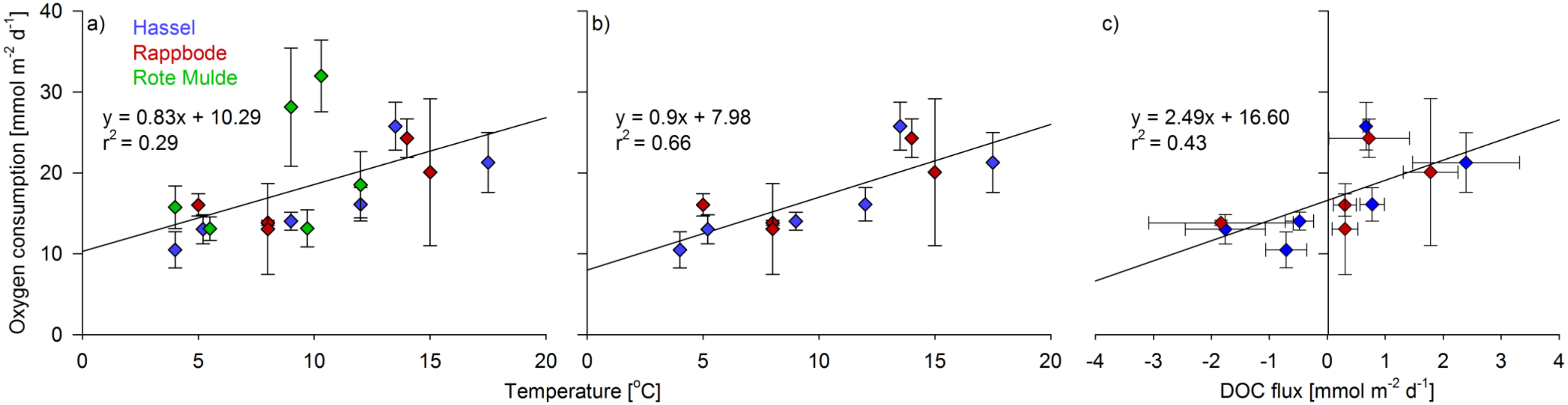

Fig. 4.4. Oxygen consumption vs temperature (a) and (b), and DOC flux (c) plots at the shallow sites under oxic conditions. Chart (a) shows data for all 3 pre-dams, and (b) and (c) only Hassel and Rappbode data. Error bars represent standard deviation of four replicates cores.

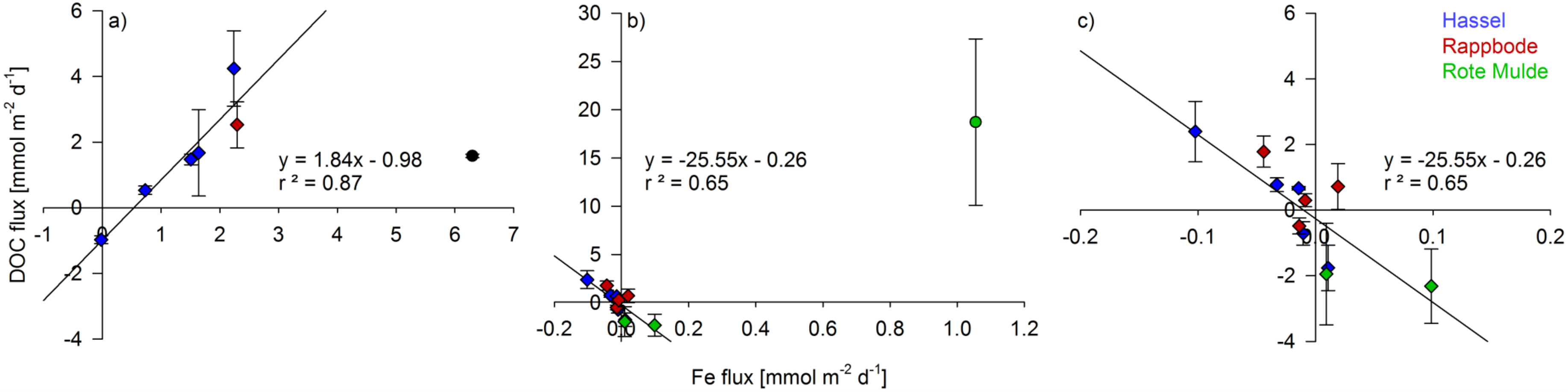

Fig. 4.5. DOC and Fe relationship; (a) deep sites (black circle point is an outlier), (b) shallow sites with outlier (green circle), c) chart (b) without the outlier. Error bars represent standard deviation of four replicates cores. Please note the different scales.

The concentration gradient between overlying water and porewater determines the direction of diffusion of solutes. There was always a higher concentration of DOC in porewater than in the overlying water for all pre-dams (Fig. 4.6). Rappbode deep site had the steepest gradient while Rote Mulde had a gradual gradient. The DOC concentration was temperature dependent in the shallow sites.

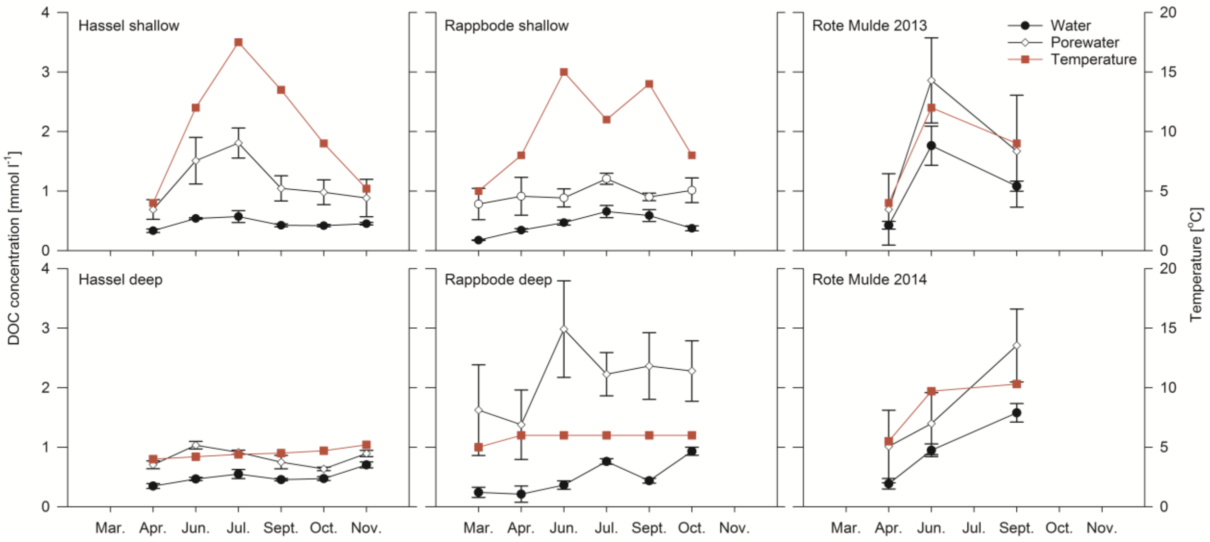

Fig. 4.6. DOC concentration in overlying water and porewater. Error bars represent standard deviation of four replicates cores.

4.5.3 DOC budgets

The DOC budgets for the pre-dams were calculated to have an overview of the annual benthic carbon exchange. Upscaling of the DOC fluxes shows that both Hassel and Rote Mulde sediments were a DOC sink while Rappbode sediment was a source (Table 4.2).

Table 4.2: Annual benthic carbon mobilization and immobilization in the pre-dams. Carbon burial is the difference between mobilized and immobilized carbon divided by the mobilized carbon.

	Hassel	**Rappbode**	**Rote Mulde**
Mobilized carbon:			
POC [tonnes yr^{-1}]	38.76	25.58	7.81
Immobilized carbon:			
DOC [tonnes yr^{-1}]	-0.18	0.23	-1.48
TIC [tonnes yr^{-1}]	8.21	9.71	1.71
CH_4 [tonnes yr^{-1}]	0.15	0.13	0
C burial [%]	79	61	97

Carbon burial was very high in the pre-dams with Rote Mulde having the highest carbon burial. The difference in oxic and anoxic DOC fluxes between Hassel and Rappbode is shown in Fig. 4.7. The seasonal fluctuations were pronounced in Hassel, which was mainly caused by seasonality of the oxic sediments.

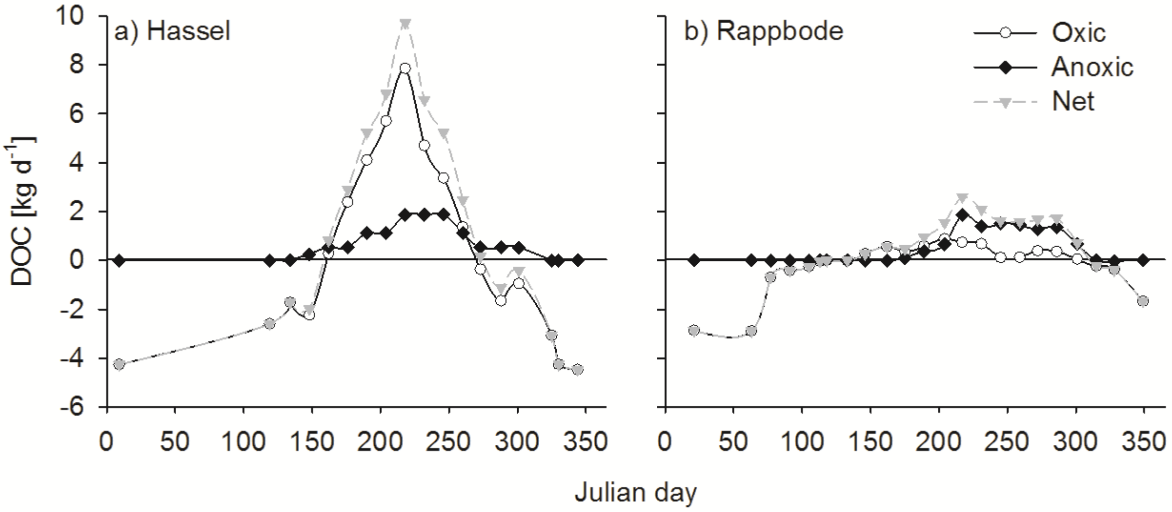

Fig. 4.7. Total benthic DOC release from sediment surface areas overlain by oxic and anoxic waters; a) Hassel, b) Rappbode.

4.6 Discussion

The general DOC flux trends under oxic and anoxic conditions were similar for all the three pre-dams. Therefore the discussion on DOC flux magnitude, drivers and mechanism raised in Chapter 4a for Hassel pre-dam is valid for the other pre-dams as well. This discussion will focus more on differences observed between the three pre-dams, and DOC quality.

4.6.1 Benthic DOC and other fluxes

Temperature dependency of DOC mobilization was observed across the pre-dams. However there was a weak DOC flux temperature dependency in Rote Mulde. This could be an indication that organic matter mineralization in Rote Mulde is controlled by other factors for example DOC quality and adsorption to mineral surfaces. Rote Mulde has higher $SUVA_{254}$ values, which indicates presence of more aromatic DOC. Sobek et al. (2005) found out that temperature dependency of carbon mineralization/carbon dioxide is more local than global. They argue that interactions of temperature and substrate as regulators can lead to a better understanding of this phenomenon. Furthermore DOC in Rote Mulde might not be bioavailable because of adsorption to mineral surfaces or particulate organic matter.

The concentration gradient between the porewater and overlying water has an influence on the DOC flux. Rappbode deep point had a steeper concentration gradient than Hassel deep site and a higher DOC flux was observed in Rappbode under anoxic conditions. The concentration gradients between porewater and overlying water in Rote Mulde do not agree to the observed high negative DOC fluxes. This could be an indication that the observed trend is controlled more by another mechanism, in this case adsorption of DOC to Fe minerals in the water column. The concentration gradient between the porewater and overlying water seemed to predict flux direction very well under anoxic conditions.

Contrastingly under oxic conditions flux direction is not entirely dependent on the concentration gradient between the porewater and overlying water, as seen through negative and positive DOC flux despite the concentration gradient favouring a positive flux. This contradiction is a result of the heterogeneity in redox conditions occurring under oxic conditions i.e. the overlying water and top sediment layer is oxic while the lower sediment is anoxic. Therefore flux direction is more influenced by thickness of the oxic sediment layer. In the oxic sediment layers diffusing ferrous Fe is oxidised to ferric Fe, which is hydrolysed to form iron hydroxides, which in turn adsorb DOC (Guggenberger et al. 1998; Skoog and Arias-Esquivel 2009) resulting in no net flux into the water. This is likely to create a relatively lower DOC concentration in this oxic layer than what is in the overlying water hence the observed negative flux. The porewater DOC concentration gradients show that seasonal patterns are governed by redox conditions but absolute fluxes depend on DOC production in the sediment.

Strong positive DOC and Fe flux correlation under anoxic conditions and strong negative correlation under oxic conditions underscores the prominence of the mechanism of desorption/adsorption of DOC from/to Fe. Furthermore the different DOC flux directions for sediments incubated at different redox conditions and change in direction of DOC flux when the redox conditions are switched (Chapter 6) indicates that the reversibility of the adsorption and desorption of DOC from Fe minerals depends on the redox conditions.

Sulphate reduction occurred in all pre-dams under both oxic and anoxic conditions. The rates of sulphate reduction in the pre-dams are on the lower end compared to rates of up to 15 mmol m^{-2} d^{-1} reported in literature (Holmer and Storkholm 2001). Sulphate production was also observed under oxic conditions and only at temperatures below $10^{o}C$. Interestingly, all cases of sulphate production coincided with a negative fluxes of DOC, which might be an indication that oxidation of sulphides contribute to the observed DOC fluxes.

4.6.2 Carbon budgets

Carbon burial was generally high in all pre-dams with Rote Mulde having the highest carbon burial. The higher carbon burial in Rote Mulde agrees with DOC quality investigations, which indicates that DOC in Rote Mulde DOC is more aromatic compared to that of the Hassel and Rappbode (Chapter 6). Hassel had a higher carbon burial than Rappbode, this could be due to the higher sedimentation (Table 4.1) observed and the higher microbial biomass of Hassel (Wendt-Potthoff et al. 2014). The higher sedimentation is probably a result of preferential utilisation of the more labile autochthonous carbon sources (Friese et al. 2014) over the more recalcitrant allochthonous carbon sources, since Hassel is eutrophic. Eutrophic water bodies have a higher carbon burial rate (Mulholland and Elwood 1982; Heathcote and Downing 2012; Anderson et al. 2014). Furthermore agriculture activities are higher in the Hassel catchment, which agrees well with the findings of Clow et al. (2015) who reported sediment carbon content ranging between 0-40% in American water bodies and linked the highest carbon burial to agricultural activities in the catchment. In another study carbon burial was found to be high in systems receiving high inputs of allochthonous carbon and also higher in sediment with low oxygen exposure time (Sobek et al. 2009). Mean sedimentation rate was higher in Hassel shallow sites, which could be an indication of a higher allochthonous carbon input. However oxygen exposure time might not be a contributing factor since Rappbode had a higher surface area under anoxia (lower oxygen exposure time) compared to Hassel yet annual CO_2 and CH_4 production was similar.

Hassel and Rappbode had similar DOC flux trends however the former is a DOC sink while the latter is a DOC source (Fig. 4.7). This striking difference was mainly because Hassel had a longer winter period and the sediments in Hassel immobilize more DOC under oxic conditions at low temperatures compared to Rappbode. The higher immobilization of DOC in Hassel seems to be more related to the sediment properties. The higher temperature dependency of DOC fluxes in Hassel implies a stronger DOC release at higher temperatures. Therefore Hassel has more potential of a higher DOC production in the event of short winters and higher temperatures. The benthic carbon emission from this study, 28.5 and 44.5 g C m^{-2} $year^{-1}$ for Hassel and Rappbode respectively, is lower than 74.9 and 87.6 g C m^{-2} $year^{-1}$ for Hassel and Rappbode respectively that has been measured in the water column (Halbedel and Koschorreck 2013). It therefore seems as if the eutrophic status of Hassel has a more impact on benthic carbon emission than in the water column.

Chapter 5: Sediment resuspension effects on dissolved organic carbon fluxes (DOC) and microbial metabolic potentials in reservoirs

Tallent Dadi, Katrin Wendt-Potthoff, Matthias Koschorreck

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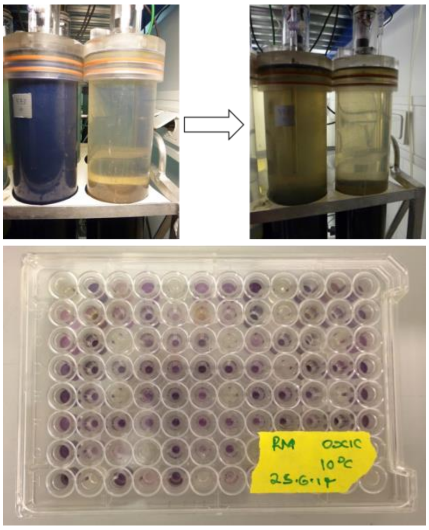

Photos: Resuspended and undisturbed sediment cores immediately after resuspension (top left) and after 24 hours (top right), and a Biolog EcoPlate™ (bottom). Photos by Tallent Dadi

Overview

Sediments in standing water bodies gradually develop, burying DOC, nutrients, metals and other solutes. The sediments are constantly disturbed mainly by wind and benthivorous fish, leading to sediment resuspension. The effects thereof in standing water bodies on benthic fluxes of DOC, metals (Fe, Mn), nutrients (N, P) and other solutes was investigated. This was achieved by manual resuspension of the upper 1 cm sediment layer in cores from three pre-dams. Also investigated was the role of heterotrophic microorganisms, which are likely introduced into water after resuspension. Mobilization and immobilization of DOC by resuspension was observed, with DOC resuspension fluxes approximately equal to 9-17 days of diffusive flux. Nutrient mobilization from the sediment after resuspension was minimal with the exception of ammonium. Resuspension increased the microbial potential to utilize organic substrates. The findings emphasize the importance of resuspension process. Resuspension also promote burial of DOC in low nutrient, Fe rich aquatic systems.

Sediment resuspension effects on dissolved organic carbon fluxes and microbial metabolic potentials in reservoirs

Tallent Dadi[*1], Katrin Wendt-Potthoff[1], Matthias Koschorreck[1]

[1] UFZ - Helmholtz Centre for Environmental Research, Department of Lake Research, Brückstr. 3a, 39114, Magdeburg, Germany

[*] Corresponding author: tallent.dadi@ufz.de

Key words: Sediment resuspension, DOC, Biolog EcoPlates™, Microbial metabolic potential

Abstract

Sediment resuspension can impact water quality in lakes and reservoirs. We investigated the effect of sediment resuspension on benthic fluxes of dissolved organic carbon (DOC), metals (Fe, Mn), and nutrients (N, P) in three drinking water reservoirs using sediment core incubations. Measurement of Fe and Mn fluxes, and determination of microbial potentials to degrade organic substrates (Biolog EcoPlates™) were employed to understand mechanisms regulating DOC exchange after sediment resuspension. A single sediment resuspension event resulted in DOC fluxes equal to 9 – 17 days of diffusive flux, which makes it a relevant process. There was variability between the reservoirs with shallow sites more likely to immobilize DOC after resuspension than deep sites. Sediment resuspension under anoxia always led to increases of DOC and metals in the overlying water. Nitrate and phosphorus were below detection limit indicating that sediment resuspension does not necessarily lead to mobilization of nutrients even under anoxia. On the contrary ammonium was released after resuspension. Sediment resuspension increased hypolimnetic microbial potentials to utilize organic substrates in both spring and summer. However microbial cells counts and biomass either remained constant or decreased in summer. Adsorption to Fe minerals seemed to play a role in DOC immobilization as evidenced by a decrease in DOC:Fe molar ratios after resuspension under oxic conditions and constant ratios under anoxia. The results demonstrate a potential for DOC immobilization mainly by Fe minerals and to some extent by benthic microbes. Therefore, sediment resuspension can be beneficial for water quality in low nutrient, iron rich systems.

Introduction

Sediment resuspension is regarded as a process with detrimental effects on water quality. It increases turbidity, which reduces light penetration (Scheffer et al. 2003). It also triggers release of nutrients trapped in the sediment porewater (Reddy et al. 1996) thereby availing limiting nutrients like phosphorus and nitrogen. Resuspension-induced unstable redox conditions can potentially affect carbon burial and cycling of nutrients (N, P, and Fe).

Sediment resuspension is caused mainly by wind and benthivorous organisms e.g. fish, bioturbation, and water level fluctuations. Wind induced resuspension is common in shallow lakes (Liang et al. 2016) but also occurs in deep lakes (Bloesch 1995; Tammeorg et al. 2013). Benthivorous fish like bream (*Abramis brama*), common carp (*Cyprinus carpio*), and roach (*Rutilus rutilus*) are well known to cause sediment resuspension as they forage for benthic invertebrates (Fischer et al. 2013; Søndergaard et al. 1990). This has led to their removal from aquatic systems, as a bio-manipulation strategy to reduce internal nutrient loading (Meijer et al. 1994; Søndergaard et al. 2008). Wind resuspension is more prone to shallow lakes while fish induced resuspension can possibly occur in deeper lakes. The two factors are not independent from each other since the presence of fish is also known to facilitate wave resuspension of the sediment by hindering sediment consolidation (Scheffer et al. 2003). Resuspension also depends on sediment quality with sandy low organic sediments less prone to resuspension compared to the soft high organic matter content sediments (Lovstedt and Bengtsson 2008). Niemisto et al. (2008) found out that sediment resuspension in summer was increased by sediment quality since the fresh sedimenting material had a low critical shear stress.

Previously sediment resuspension has been addressed in the light of nutrients; however, there are emerging solutes of concern e.g. dissolved organic carbon (DOC). Dissolved organic carbon has been increasing in aquatic systems in the Northern hemisphere, a trend which is predicted to continue and could severely alter light regimes in aquatic systems (Evans et al. 2005). It is a problem for drinking water treatment because it requires more coagulants to be removed (Eikebrokk et al. 2004), reacts with disinfection agents to form carcinogenic trihalomethanes (Gough et al. 2014), and causes inadequate disinfection due to immobilization of disinfection agents, and fouling of filtration membranes (Carroll et al. 2000). While several studies addressed the turnover of DOC in surface waters (Jones et al. 2015), less is known about the role of sediments for aquatic DOC. A recent study showed that sediments can be both a source and a sink for DOC and that the diffusive DOC flux at the sediment water interface is controlled by redox dependent sorption to iron minerals (Dadi et al. 2016). However, diffusion is probably not the only transport mechanism for DOC between sediment and water.

Resuspension mixes porewater with elevated solute concentrations into the water and thus, increases concentration of solutes in the water. In marine systems, Koschinsky et al. (2001) found that DOC increased after resuspension due to the mixing of overlying water with porewater with an elevated DOC concentration. However, a recent study showed that resuspension of sediment may also lower the DOC concentration in the water (Dadi et al. 2016). The introduction of mineral particles into water may enable absorption of DOC and subsequent sedimentation. We further hypothesised that resuspension has another, indirect effect on hypolimnetic DOC: it likely transfers benthic bacteria into the hypolimnetic water (Ritzrau and Graf 1992; Wainright 1990), which may enhance microbial degradation of DOC.

We performed laboratory experiments with undisturbed sediment cores from drinking water reservoirs to determine how resuspension events affect the direction and magnitude of the flux of DOC and other solutes at the sediment water interface. Iron is known to adsorb phosphorus and organic matter. However, this is influenced by the redox potential. Adsorption will occur under oxic conditions while desorption occurs under anoxia. Based on this redox sensitive adsorption mechanism to Fe minerals we hypothesise that sediment resuspension under oxic conditions decreases the DOC concentration in the water.

Material and methods

Study area and sampling

The study was carried out in three drinking water reservoir pre-dams in Germany; Hassel, Rappbode, and Rote Mulde (Table 1). Hassel and Rappbode pre-dams are situated in the Harz Mountains (51.74° N, 10.89° E), in central northern Germany, while the Rote-Mulde pre-dam is located in the Vogtland, Saxony, Germany (50.40° N, 12.38° E). Further information on the pre-dams Hassel and Rappbode can be found in Wendt-Potthoff et al. (2014) and on Rote Mulde in Wobus et al. (2003). Rappbode and Hassel pre-dam contained benthic feeding fish; roach, bream, and carp. Carp was stocked and annual catch in both pre-dams had been around 300 kg in the period 1994 – 2004 (Björnsen Beratende Ingenieure GmbH 2012). No information was available about fish in the Rote Mulde pre dam.

In Hassel and Rappbode pre-dam we had two sampling sites each: one at the deepest point, which became anoxic during stratification and one in the riverine section of the reservoirs, which was oxic most of the time. The shallow Rote Mulde pre-dam was well mixed and oxic all year round. Hassel and Rappbode were selected based on the difference in trophic state, Hassel is eutrophic and Rappbode is mesotrophic. Rote Mulde was selected in addition to the other two because of its higher DOC concentration.

Table 1: Pre-dam morphometry, hydrological and water quality properties and sampling periods. ^{1} refers to shallow site and ^{2} refers to deep site.

Pre-dam	**Hassel**	**Rappbode**	**Rote Mulde**
Volume [1000 m^3]	1448	1146	62
Mean depth [m]	5.0	5.7	0.6
Residence time [d]	65	52	6
Catchment area [km^2]	44.6	47.6	5.4
Catchment land use;			
Forest	37%	72%	98%
Grasslands	33%	22%	1%
Agriculture	25%	2%	0%
Other	5%	3%	1%
pH	6.5 - 9.6	6.5 - 8.4	5.0 - 6.9
DOC [mmol l^{-1}]	0.3 - 0.6	0.2 - 0.6	0.5 - 2
Fe [mmol l^{-1}]	0.001 - 0.012 ^{1} 0.009 - 0.241 ^{2}	0.003 - 0.010 ^{1} 0.014 - 0.048 ^{2}	0.008 - 0.037^1
Sampling sites	Shallow (3.5 m), Deep (13 m)	Shallow (4 m), Deep (16 m)	Shallow (3.5 m)

At each site and date 4 replicate cores were sampled. The cores were covered with stirrer heads and transported in insulated boxes to maintain *in situ* temperatures. For detailed description of sediment core handling and the incubation procedure refer to Dadi et al. (2015).

Sediment resuspension experiment

The undisturbed sediment cores (9 cm diameter) with an average water height of 24 cm were incubated at *in situ* temperature and oxygen conditions, in climate chambers. First, the cores were incubated for 14 days to measure diffusive solute fluxes. During that time 4 samples were taken and the diffusive flux of various solutes was calculated from the linear concentration increase in the water over time.

Sediment resuspension was then carried out immediately after the last sampling of the incubation experiment by manually disturbing approximately the upper 1 cm sediment layer using a glass rod. Prior to resuspension, all oxic cores were bubbled with oxygen to saturation to prevent anoxic conditions. For anoxic cores oxygen contamination was prevented by switching off the stirrers during the resuspension, which was done within 30 seconds. After gas bubbles were removed, the cores were closed and stirrers for anoxic cores switched on. The cores were incubated for a period of 24 hours in the dark and during that time oxygen consumption in oxic cores was continuously measured with optical oxygen sensors (Pyro Science, Germany). From prior turbidity tests we found out that turbidity of resuspended cores became constant after 18 hours hence a 24 hour incubation period ensured settling of particles. After approximately 24 hours the overlying water from the resuspended cores was sampled and analysed for DOC, NH_4^+, NO_3^-, soluble reactive phosphorus (SRP), SO_4^{2-}, Fe, and Mn. Analysis for DOC, NO_3^-, SO_4^{2-}, Fe, and Mn using standard methods (Dadi et al. 2016). Ammonium was analysed by using an ammonium ion-selective electrode with a separate lithium acetate reference electrode (ELIT 8051 and ELIT 003n; Nico2000 Ltd.,UK). Soluble reactive phosphorus (SRP) was analysed photometrically (Cary 60 UV/Vis spectrophotometer; Agilent, Malaysia) based on the method of (Laskov et al. 2007). Finally all cores were sectioned at the following depths: 0-1, 1-3 and 3-5 cm. Part of these samples was used to collect porewater by centrifugation at 3750 rpm for 15 min. The collected porewater was analysed for all parameters mentioned before. The remaining sediment sample was used for water content and loss on ignition analysis

The resuspension flux was calculated as the difference between the concentration before and after resuspension divided by the sediment core surface area and expressed on per event basis. The resuspension fluxes of DOC were correlated (Pearson’s correlation, SPSS version 22) with resuspension fluxes and porewater concentration of other solutes, temperature, oxygen condition, and sediment organic matter content.

Repeated resuspension experiment

A repeated resuspension experiment was done only with Rote Mulde sediments in September 2014. The aim of the experiment was to investigate if a series of resuspension over time would have an effect on solute flux magnitude and direction. The experiment design is shown in Fig. 1. Resuspension was carried out as described in the previous section. Water exchange was carried out by siphoning the overlying water to a water level of 5 cm water height which was about 20% of the total overlying water volume. This was done to prevent sediment resuspension during refilling especially for core 4 which was supposed to remain undisturbed for the duration of the experiment. The cores were carefully refilled by a gravity method using a silicon tube with an upward facing loop, to allow slow refilling without sediment disturbance. Sample volume after each sampling event was replaced by bottom water. The concentrations of various solutes in the bottom water were analysed for each sampling day and this data was used to correct for the sample volume related concentration changes in the cores.

Core	Week 0	Week 1	Week 2	Week 3	Week 4	Week 5
1	R	R	R	WE & R	WE & R	WE & R
2	R	X	X	WE & R	WE	WE
3	R	R	R	WE & R	WE & R	WE & R
4	X	X	X	WE	WE	WE

Treatments
R – resuspended
WE – water exchange
X – no treatment

Fig. 1. Repeated resuspension experiment design. Please note that core 1 and 3 received the same treatment while core 4 was the control (not resuspended).

Benthic microbial metabolic potential and bacteria enumeration

The objective of this analysis was to investigate the effect of sediment resuspension on microbial carbon substrate utilisation pattern in the hypolimnion. We used Biolog EcoPlates^{TM} (Biolog, Inc., Hayward, California) to determine the potential of microbes to utilize known dissolved organic substrates. The Biolog EcoPlates consist of 96 wells, with 31 substrates and a control (no substrate) replicated 3 times. The substrates comprised 6 amino acids, 10 carbohydrates, 9 carboxylic acid, 2 amines, and 4 polymers (Christian and Lind 2007).

The metabolic potential without resuspension was determined in bottom water sampled by a water sampler. To assess the effect of resuspension, a composite sample collected from the four replicate cores after resuspension was used. All incubations were conducted at *in situ* oxygen concentration and temperature. Oxic Biolog plates were prepared by inoculating 150 µl of sample into each well of the Biolog EcoPlate. For anoxic Biolog plates, a sterile sodium sulphide stock (1000 mg l^{-1}) solution was added to the sample (2/98% v/v) to give a concentration of 20 mg l^{-1} sulphide in the sample of which 150 µl was pipetted into each well of the Biolog EcoPlate. The anoxic Biolog plates were immediately covered with Roth ThinSeal$^{™}$ adhesive sealing clear film for microplates. Both oxic and anoxic Biolog plates were allowed to stand for 30 minutes before the initial measurement of the optical density at 595 nm (OD_{595nm}) using a Multiskan RC (Thermo Labsystems) microtiter plate reader. The anoxic Biolog plates were placed in Merck special anaerobic incubation bags and a moistened Merck Microbiology Anaerocult® A mini gas generator system for anoxic incubation was inserted in the bag together with a Merck Anaerotest® strips for detection of anaerobic conditions. The Biolog plates were then incubated at the respective temperature in the dark and were measured daily within the first 3 days and 2-3 times a week thereafter, until the average well colour development (AWCD) was constant. A control correction was applied to each well by subtracting the mean OD_{595nm} of the control well. The AWCD was plotted against time and the resulting curve was used to determine the peak AWCD. To compare the different experiments results the peak AWCD was divided by the duration of the incubation at peak AWCD to get an AWCD rate (OD_{595nm} d^{-1}). A regression analysis (SPSS version 22) of the AWCD rate was carried out, with temperature, oxygen condition, resuspension, sampling site and substrate group as the independent variables.

Total bacteria enumeration was carried out for selected samples. Samples were fixed with 5% Lugol solution and stored in brown glass vials. One millilitre of the sample was vacuum filtered through a Whatman Nuclepore filter (0.2 µm) and then 150 µl of dilute (1:250) SYBR Green solution was pipetted on the filter and allowed to stand for 15 minutes before it was vacuum filtered. The enumeration and analysis of the bacteria was carried out using an Axiolab epifluorescence microscope at 1000x magnification equipped with the New Porton Grid G12 (May 1965). Bacteria were enumerated in 20 grids and cell volume was determined by noting the length and width of 50 bacterial cells on the filter. Biomass was calculated using the (Simon and Azam 1989) method. All statistical significance tests and multiple regression analysis were carried out using SPSS version 22. Multiple regression analysis was done to compare the influence of oxygen condition, temperature, resuspension and samplings site on AWCD.

Results

Background properties of the pre-dams

The pre-dams were selected on the basis of differences in trophic state and DOC concentration. We also found that the sediments differed in their organic content. Loss on ignition (LOI) was similar for Hassel and Rappbode shallow sites. However it was relatively lower than that of the deep sites, which were also similar (Table 1). Rote Mulde sediment contained twice as much organic matter as the shallow sites of Hassel and Rappbode. Overlying water pH for Hassel and Rappbode sites was in the neutral range while that of Rote Mulde was slightly lower. The pH may play a role in the availability of DOC due to its effect on surface charge of DOC compounds. The water content followed a similar trend like LOI, however, the water content of the Hassel and Rappbode deep sites was comparable to that of Rote Mulde, which is a shallow site. Microbial biomass in the sediment was significantly higher in June than in March. It was similar at Rappbode shallow and deep site but significantly higher in Rote Mulde. The deep sites in Hassel and Rappbode were at times anoxic during summer and autumn (Table 2).

Porewater concentrations

Porewater is known to be rich in solutes. Therefore, sediment resuspension is expected to release solutes into the overlying water. Fig. 2 compares the overlying water concentration of solutes before resuspension and mean porewater concentrations of the uppermost 5 cm of sediment. Dissolved organic carbon was always higher in the porewater compared to the overlying water for all the pre-dams and sites. Thus, there was always the

Table 2: Resuspension experiment background information and sediment quality parameter for the 3 pre-dams. Note [a] is under oxic conditions, [b] is under anoxic conditions, [c] is before resuspension, [d] is after resuspension, and [*] March and June combined for Rappbode shallow and Rote Mulde, and only March for Rappbode deep site. Concentration refers to porewater concentration.

Pre-dam	**Hassel**		**Rappbode**		**Rote Mulde**
Site	**Shallow**	**Deep**	**Shallow**	**Deep**	**Shallow**
Resuspension dates (oxic = not bold, **anoxic = bold**)	2013: Apr., Jun., Jul., Sept., Oct., Nov.	2013: Apr., **Jun., Jul., Sept., Oct., Nov.**	2014: Mar., Apr., Jun., **Jul.**, Oct.	2014: Mar., Apr., Jun., **Jul.**, **Oct**.	2013, 2014: Apr., Jun., Sept.
LOI [%]	15	26	13	20	41
Water content [%]	87	97	79	94	95
Overlying water pH	7.00 ± 0.33[a]	6.66 ± 0.09[a] 6.89 ± 0.08[b]	7.19 ± 0.15[a] 7.44 ± 0.11[b]	7.23 ± 0.34[a] 7.31 ± 0.01[b]	6.14 ± 0.33[a]
Microbial biomass[*] [μg C ml^{-1}]	Not analysed	Not analysed	0.06 ± 0.02[c] 0.08 ± 0.03[d]	0.04 ± 0.002[c] 0.08 ± 0.004[d]	0.11 ± 0.08[c] 0.22 ± 0.08[d]

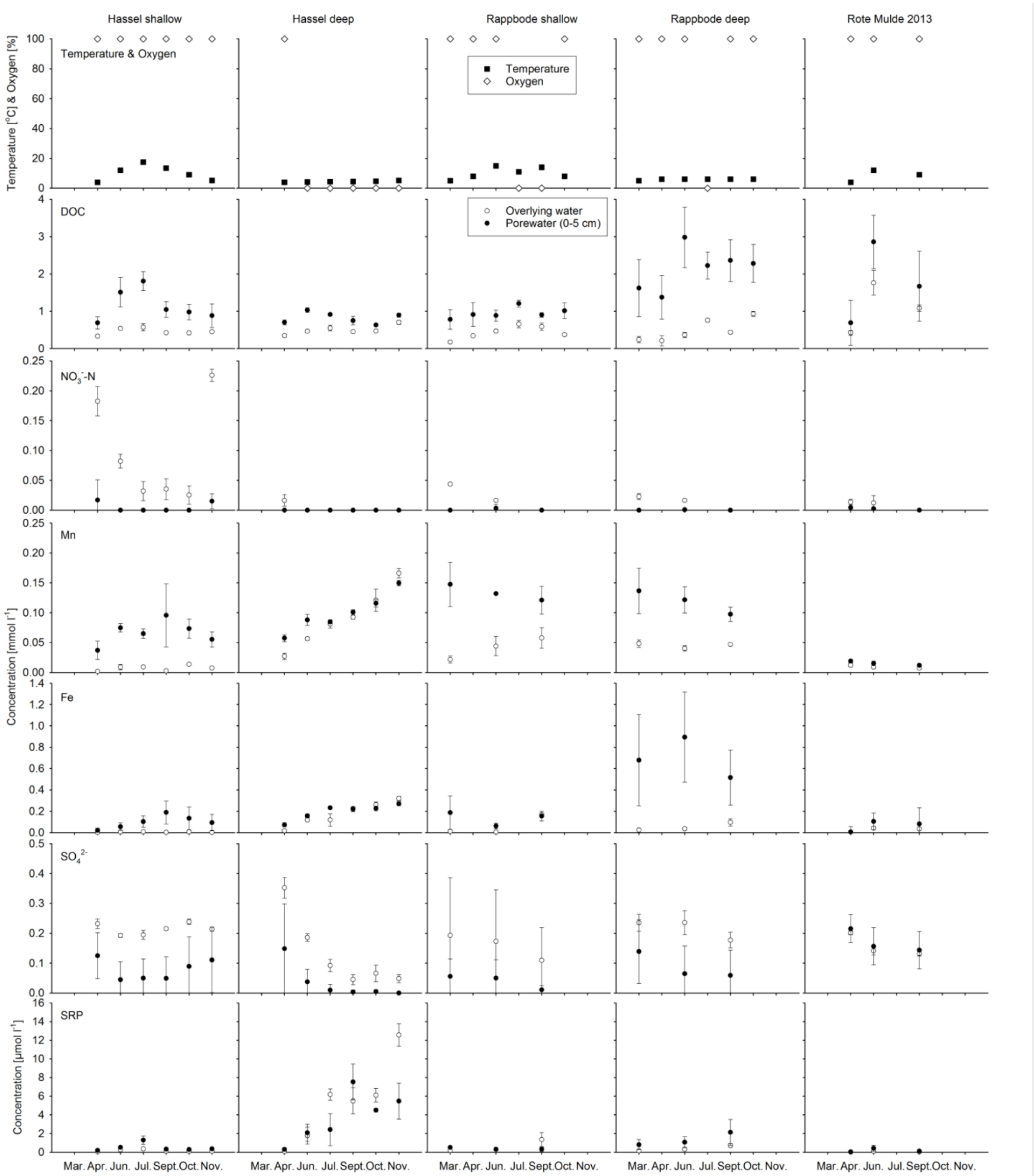

Fig. 2: Porewater concentration of DOC, NO_3^--N, Mn, Fe, SO_4^{2-}, and SRP for overlying water at the start of resuspension and mean porewater for the 3 sectioned layers (0-1, 1-3, 3-5 cm), and temperature and oxygen during resuspension. Error bars for overlying water represent standard deviation of 4 replicate cores while those for porewater represent standard deviation of the 3 layers. Please note concentration of SRP is expressed in [µmol l^{-1}] while that of all the other solutes is in [mmol l^{-1}].

potential for the release of DOC during resuspension. We would expect highest DOC release at the Rappbode deep site, where the porewater concentration of DOC was highest. Nitrate concentrations in the overlying water were negligible except for the Hassel shallow site. Manganese and Fe concentration had a similar trend to that of DOC in both overlying water and porewater. However, the concentration gradient for the Hassel deep site was minimal. Sulphate unlike other solutes was higher in the overlying water than the porewater for all pre-dams and sites, indicating sulphate reduction in the sediment. Soluble reactive phosphorus in both overlying water and porewater was very low for all pre-dams and sites except for Hassel deep site. Figure 2 also shows the seasonality effects (both temperature and oxygen concentration) on the solutes concentrations in both overlying water and porewater. Generally, porewater concentrations (with the exception of sulphate) were higher during summer, suggesting a higher release potential during the warm season.

Resuspension fluxes of DOC and other solutes

Sediment resuspension effects on DOC fluxes varied among the pre dams (Fig. 3). Hassel pre-dam exhibited a DOC uptake trend under oxic conditions and a DOC release under anoxic conditions. However, in September and October the deep site deviated from this pattern. Rappbode sediment, on the other hand released DOC after resuspension regardless of the redox conditions. Rote Mulde, which was oxic for all experiments showed a similar trend to that of Hassel under oxic conditions, but with a relatively higher magnitude. The sediment core variability for all the pre-dams was high as indicated by the error bars.

At Hassel and Rappbode, Fe and Mn were released after resuspension. However, there was a deviation from this trend at the deep sites: Hassel (April, July) and Rappbode (September) for Fe, and Hassel (November) and Rappbode (September) for Mn (Fig. 4 b, c). In Rappbode there was a clear positive effect of resuspension on Mn while in Hassel effects on Fe were more pronounced. A slight negative effect of resuspension on dissolved metals was observed in Rote Mulde (Fig.4 d). Sulphate was released under oxic conditions at all sites and was consumed under anoxic conditions (Fig.4).

Surprisingly, resuspension had little effect on dissolved nutrients (Fig. 4 a, e, f). Effects were mostly visible in the nutrient rich Hassel pre-dam. Liberation of NH_4^+ under anoxic conditions was observed while under oxic conditions resuspension resulted in a decrease of nitrate. A clear effect on SRP was only visible under anoxic conditions at the deep site in Hassel. However, this effect was not consistent: in June and November resuspension increased the SRP concentration in the water while in September and October it lowered the SRP concentration.

Bacterial biomass in the sediment was higher after resuspension for all sites (Table 2). Microbial biomass was significantly higher after resuspension in March for all three sites. In June biomass before and after resuspension was not significantly different in Rappbode shallow site but it was significantly lower after resuspension in Rote Mulde.

DOC resuspension fluxes significantly correlated with most of the measured parameters suggesting a common mechanism of mobilisation

(Table 3). DOC resuspension fluxes correlated negatively with oxygen concentration and sediment organic matter content (Table 3). When the data were split into oxic and anoxic situations, highly significant correlations with metal fluxes were apparent only under oxic conditions.

Table 3: Dissolved organic carbon resuspension flux Pearson's correlations with measured parameters; all data, oxidized, and reduced conditions. Please note: Table only shows data for which there was a significant correlation for at least one of the data sets. * Correlation is significant at the 0.05 level (2-tailed), ** correlation is significant at the 0.01 level (2-tailed), NS = not significant, NA = Not applicable.

Parameter	**All data**	**Oxic data**	**Anoxic data**
DOC concentration	$-0.30^{n=111}$	$0.35^{n=80}$	NS
O_2	$-0.40^{*n=111}$	NA	NA
Fe flux	$0.46^{**n=79}$	$0.38^{**n=59}$	$0.56^{*n=20}$
Mn flux	$0.31^{**n=79}$	$0.46^{**n=59}$	NS
Mn concentration	$0.66^{**n=80}$	$0.69^{**n=59}$	NS
SO_4^{2-} concentration	$-0.33^{**n=80}$	NS	NS
SRP flux	NS	$0.26^{*n=59}$	$-0.72^{**n=20}$
Temp	NS	NS	$0.42^{*n=31}$
LOI	$-0.48^{**n=110}$	$-0.56^{**n=79}$	$-0.48^{*n=31}$
pH	$0.62^{**n=111}$	$0.61^{**n=80}$	$0.46^{**n=31}$

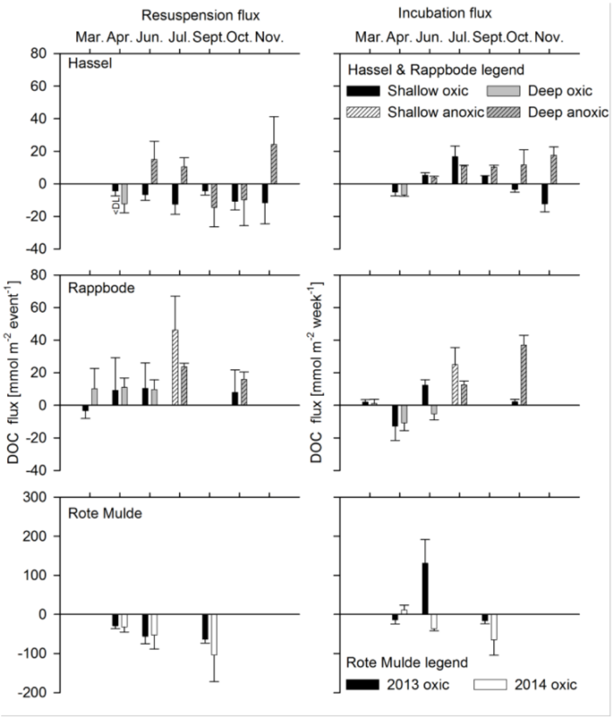

Figure 3: Resuspension fluxes of DOC (left panels) compared to the diffusive fluxes (right panels) for the three pre-dams. Error bars represent standard deviation of 4 replicate cores. Please note the difference in scales for that of Hassel and Rappbode, and the one for Rote Mulde. The incubation flux for Hassel is from Dadi et al. (2016). Please note resuspension fluxes below detection limit are marked with a <DL label.

Metabolic potential of hypolimnetic microorganisms

Resuspension altered the metabolic properties of the microbial community in the water overlying the sediment cores (Fig. 5). In most cases, enzymatic activities were higher after resuspension. All the substrate groups presented on the Biolog EcoPlate were utilized under all the different conditions tested: sites, temperature, oxygen condition and resuspension. However there were some differences in the substrate utilization pattern: the AWCD under oxic condition was higher than under anoxic conditions and higher temperature resulted in higher AWCD compared to lower temperatures. In general polymers were the most utilisable substrate group while carboxylic acids were the least utilisable substrate group. A multiple regression analysis showed that 66% of variability in AWCD can be explained by oxygen condition, temperature, resuspension, and site. Regression analysis of the individual variables showed that, of that temperature, oxygen, resuspension and site explained 52, 24, 9, and 2 % respectively.

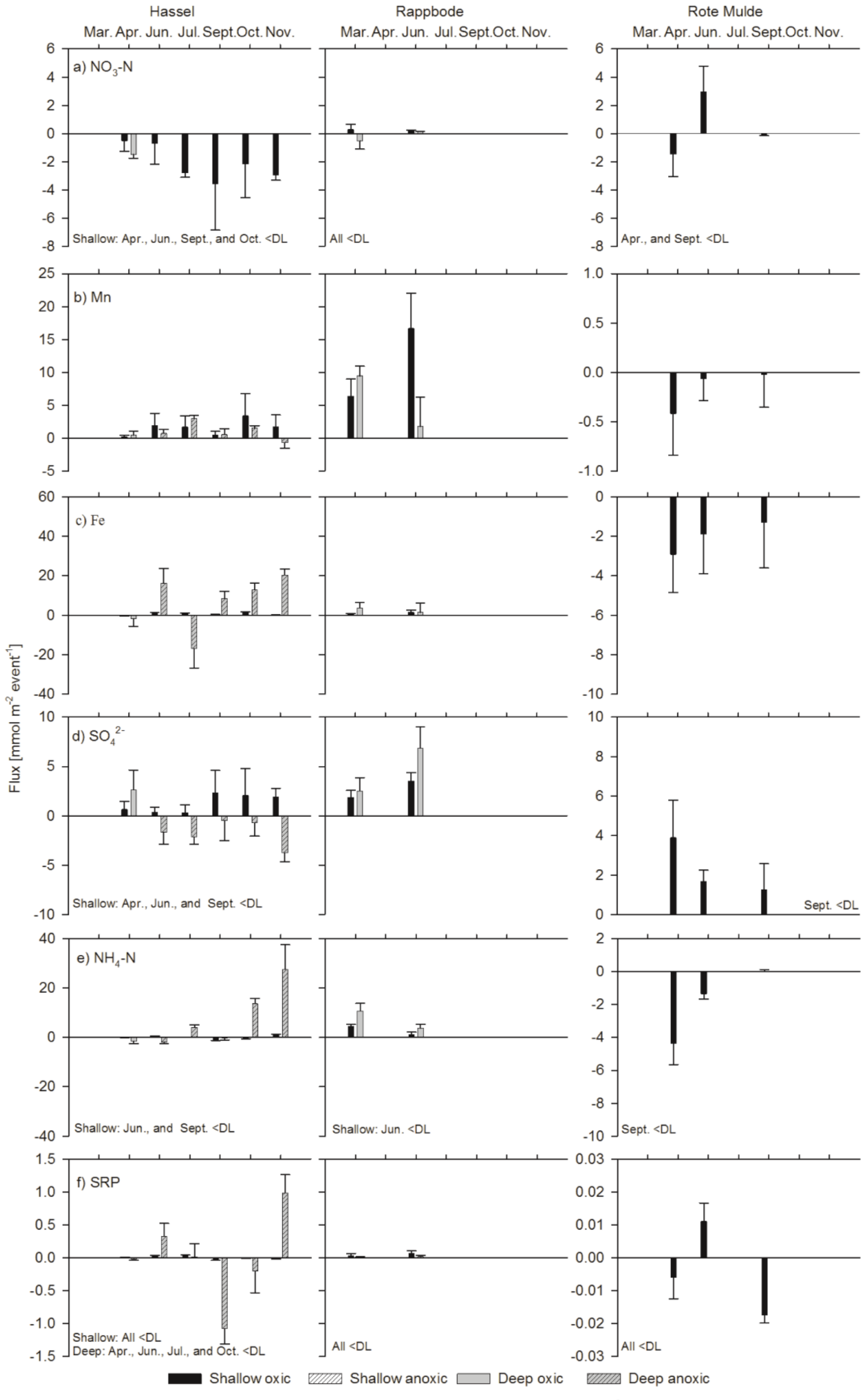

Figure 4: Resuspension fluxes of other solutes; (a) NO_3^--N (b), Mn, (c) Fe, (d) SO_4^{2-} , (e) NH_4-N, and (f) SRP, for the three pre-dams. Error bars represent standard deviation of 4 replicate cores. Please note the Hassel and Rappbode have one scale and Rote Mulde has a different scale. There was no NO_3-N at the time of resuspension in Hassel deep site from June to November. Please note all fluxes below detection limits are stated on the bottom left of each chart.

Surprisingly, the cell count data showed a different trend to that of microbial potential to utilise organic substrates. Cell counts were higher after resuspension only in April at Rote Mulde and March at Rappbode shallow and deep sites (Fig. 6).There was also a significant effect at the deep site in June but the difference between the before and after was very big prompting us to consider this data point as an outlier. In April the cell counts after resuspension were nine times higher for Rote Mulde and doubled at both Rappbode deep and shallow sites. In June cell counts after resuspension were 17% higher for Rote Mulde and 32% lower for Rappbode shallow site. Comparisons between sites show that there was no significant difference in cell counts between Rote Mulde (April), and Rappbode shallow and deep site (March) before resuspension but there was a significant difference after resuspension. Cell counts in Rappbode shallow and deep site were similar in March.

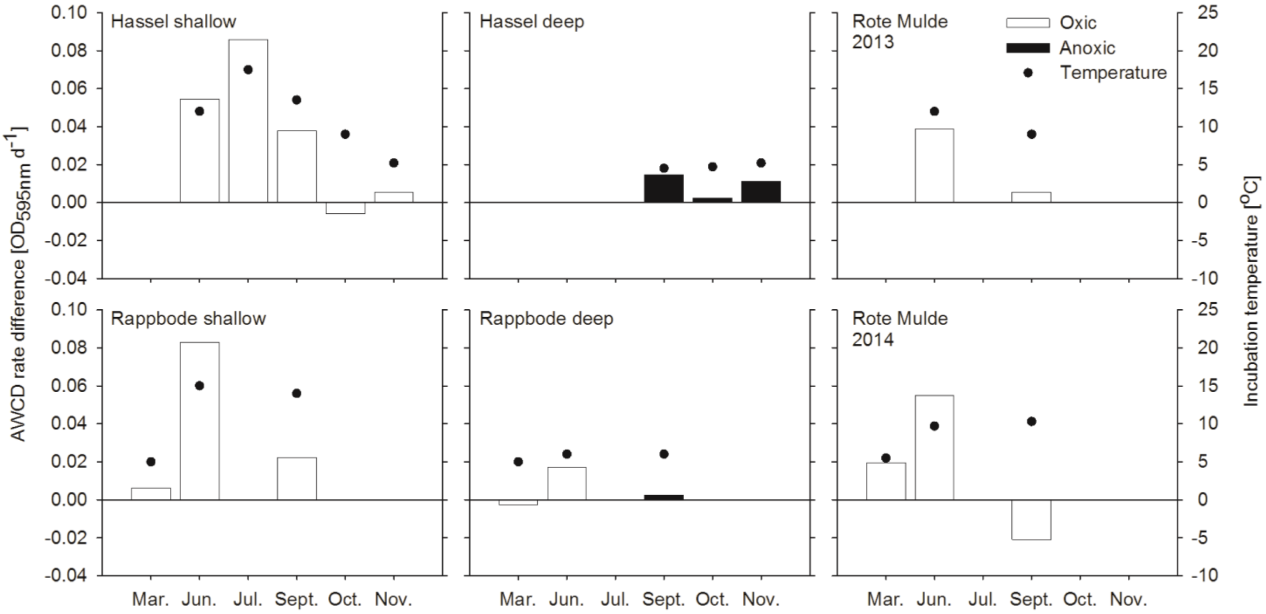

Figure 5: AWCD rate difference between after and before resuspension of the 31 substrates under oxic and anoxic conditions; Top (2013): Hassel shallow and deep site, and Rote Mulde shallow site, Bottom (2014): Rappbode shallow and deep site, and Rote Mulde shallow site. Positive AWCD rate difference indicates that AWCD was higher after resuspension and negative values indicate that AWCD was lower after resuspension.

Change in DOC concentration can imply mobilization (positive flux) from or immobilization (negative flux) by the sediment. In order to determine the relevance of microbial processes we calculated the ratio of change in microbial biomass (ΔBC) and change in DOC concentration before and after resuspension (ΔCC). From our data this gives rise to 3 scenarios; 1) positive ΔBC and negative ΔCC (bacteria C consumption contributes to C immobilization), 2) positive ΔBC and positive ΔCC (bacteria C consumption reduces C mobilization), and 3) negative ΔBC and positive ΔCC (bacteria C contributes to C mobilization). Scenario 1 applies to Rappbode shallow site in March (0.41), Rote Mulde in April (0.29), and June (0.03), and Scenario 2 applies to Rappbode deep site in March (0.06). Scenario 3 applies to Rappbode shallow site in June (0.14).

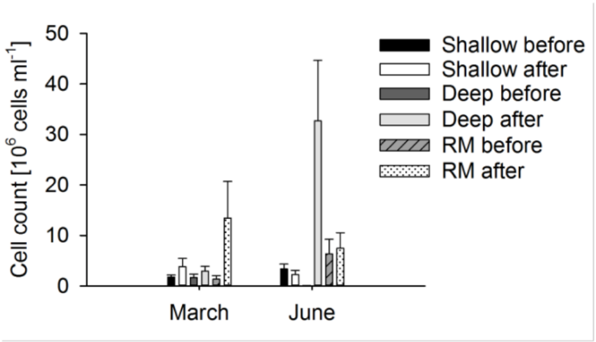

Figure 6: Cell count under oxic conditions for Rappbode shallow and deep site and Rote Mulde (RM), before and after resuspension.

Repeated resuspension

If surface adsorption plays a role for resuspension effects, we would expect decreasing effects of consecutive resuspension events. Repeated resuspension of sediment cores resulted in decreasing effects of consecutive resuspension only when the overlying water was not changed (Fig. 7 left, R1-3). Repeated resuspension with water exchange (Fig. 7 left, R4-5) actually resulted in higher resuspension effect magnitudes, similar to that of the initial resuspension (Fig. 7 left, R1). The decreasing effect was only observed at the third resuspension (Fig. 7 left, R6). Cores that were resuspended every week (core 1 and 3) always had a higher resuspension effect than core 2, which was resuspended once every 3 weeks. (Fig. 7 left, R2, 3, 5, 6). We also calculated the incubation fluxes between resuspension periods (Fig. 7 right) and found a similar trend to the resuspension fluxes. The incubation fluxes were higher in the resuspended cores than the control (Fig. 7). This implies that resuspension also had a long lasting effect on the benthic DOC flux. In contrast there was minimal net change in DOC flux in the sediment core which was not resuspended (core 4), even after the exchange of overlying water. The DOC concentration in the water for exchange was constant. The correlation between DOC concentration (at the start of resuspension) and the resuspension flux was: R^2 = -0.21, 0.05, -0.78, and 0.00 for cores 1, 2, 3, and 4 respectively. This implies that the resuspension effect in cores resuspended every week (core1 and 3) was more dependent on the DOC concentration compared to the less resuspended core 2 and the control, core 4.

We also observed a decline in pH (from 6.2) within the first 3 resuspensions by 1.3, 1.0 1.5 and 0.6 units for the core 1, 2, 3, and 4 respectively. The pH increased in the last 3 resuspensions with water exchange however it still remained lower than the exchange water pH (6.2) by 0.5, 0.2, 0.7, and 0.3 for the core 1, 2, 3, and 4 respectively.

Assuming the reduction in pH was caused by the hydrolysis of newly formed ferric iron from ferrous iron oxidation (Equation 1), we indirectly estimated the resulting concentration of ferrous iron oxidation.

$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$ [Equation 1(Stumm and Morgen 1996)]

The resulting Fe fluxes were 0.03, 0.02, 0.10, and 0.01 mmol m^{-2} d^{-1} for the Core 1, 2, 3, and 4 respectively.

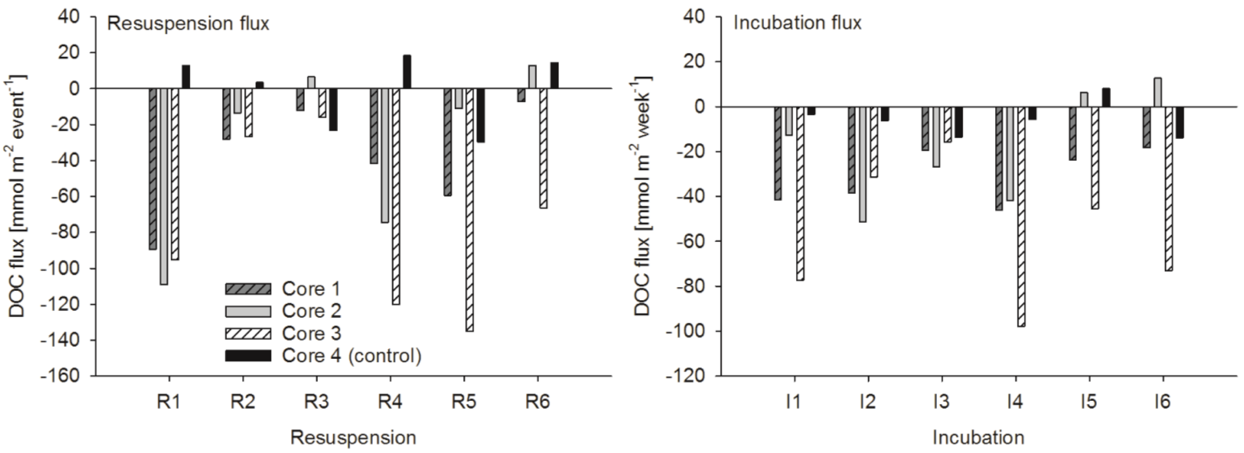

Figure 7: Repeated resuspension flux (left) and incubation flux between the resuspension (right) for DOC in Rote Mulde sediment in November 2014. Resuspension R1, 2, 3 were done without change of the overlying water while R4, 5, 6 were followed by exchange of overlying water. Core 1 and 3 were resuspended for all the six resuspensions, core 2 was only resuspended in R1 and R4, core 4 was not resuspended at all.

Discussion

Direct resuspension effects

We carried out manual resuspension of sediment cores and this generated peak turbidity of up to 57 NTU. This is similar to the fish induced turbidity of up to 70 NTU that was observed in other studies (Goetz et al. 2014; Roberts et al. 1995). The effect of single resuspension events was equal to 9 – 17 days of diffusive flux for DOC. Resuspension events can cause abrupt changes to solute exchange at the sediment water interface in both direction and magnitude. A similar trend was observed in other studies; Reddy et al. (1996) found out that resuspension fluxes of NH_4^+ and SRP were higher than the diffusive fluxes in the hypereutrophic Lake Apopka, while Søndergaard et al. (1992) found the resuspension fluxes to be 20-30 times higher than fluxes from undisturbed sediment. Our results show that resuspension does not only affect nutrients but also DOC exchange at the sediment water interface.

Site and time dependent variability was evident in Hassel pre-dam but not in Rappbode pre-dam. The difference in DOC fluxes magnitude and direction after resuspension between the shallow and deep sites in Hassel seemed to be influenced by redox conditions. Resuspension effects on fluxes of DOC under anoxia were the same for the investigated sites however they differed among the three lakes under oxic conditions. The DOC sink effects observed in Hassel and Rote Mulde and source effects in Rappbode could be due to differences in sediment quality. The texture of the Rappbode shallow site sediment was coarser compared to that of Hassel shallow site and Rote Mulde. Hassel shallow site also had coarser sediment compared to Rote Mulde which could explain the 2- 5 times higher DOC sink effect in Rote Mulde. Sediment quality has been shown to have an effect on resuspension (Lovstedt and Bengtsson 2008; Niemistö et al. 2012). Increase of DOC concentration after resuspension is expected mainly due to high porewater concentration as observed in this study and another study

Koschinsky et al. (2001). Furthermore resuspension in the repeated resuspension experiment increased the diffusive flux. A possible explanation is that resuspension equalized the porewater DOC concentration in the uppermost centimetre of the sediment, which resulted in a higher porewater concentration at the very surface. The steeper concentration gradient at the sediment water interface then caused the higher diffusive flux.

The role of sediment resuspension in nutrient loading seems to depend on the trophic state of the lake. In other studies performed in eutrophic and hypereutrophic shallow lakes, sediment resuspension increased nutrient concentrations (de Vicente et al. 2010; Gibson et al. 2015; Holmroos et al. 2012). Our results show that most SRP fluxes were below the detection limit, even: 1) under anoxic conditions, and 2) in the eutrophic Hassel pre-dam. Morgan et al. (2012) found out that in eutrophic FeS rich sediments, SRP peaked within 1 hour of resuspension and then declined to very low or undetectable limits, a trend they attributed to immobilization of SRP by freshly formed Fe oxyhydroxides. Our results also show that SRP release >0.5 mmol m^{-2} $event^{-1}$ occurred at the deep sites, under anoxic conditions. It has no importance in the shallow parts of the lake, which *in situ* are more prone to wind and fish induced resuspension. Nitrate was also below detection limits, which is contrary to the increased nitrate concentration observed in other studies (Tengberg et al. 2003). Ammonium release after resuspension occurred mostly under anoxic conditions and oxic conditions with temperatures <10^{o}C in Hassel and Rappbode. In contrast Rote Mulde had reduced NH_4^+ concentration in the overlying water. Ammonium release has been observed in other studies (Müller et al. 2015; Nowlin et al. 2005) and is attributed to mineralisation of organic nitrogen under both oxic and anoxic conditions. Ammonium is likely always produced in the sediment, however, the rate of consumption is higher under higher temperature (Saad and Conrad 1993) hence the lower concentration following resuspension under high temperature conditions. This could also be explained by adsorption of NH_4^+ to clay minerals (Rožić et al. 2000). To summarise, our results indicate that nutrients release after resuspension can be very low in nutrient poor drinking water reservoirs.

Indirect resuspension effect

In most cases resuspension resulted in a faster utilisation of organic substrates indicating that there was an enhancement of the organic substrate utilisation after resuspension. Heterotrophic bacteria are abundant at the sediment surface (Liikanen and Martikainen 2003), therefore resuspension introduces them to the water column leading to increased carbon mineralization. Microbial abundance increased after resuspension in March (Fig. 6). Surprisingly in June the Rappbode and Rote Mulde shallow sites had similar cell counts before and after resuspension but a faster substrate utilisation after resuspension. The microbial biomass in the water also decreased after resuspension at both sites. Increased bacterial abundance has been observed after resuspension in other studies (Garstecki et al. 2002; Ritzrau and Graf 1992; Wainright 1990; Ziervogel et al. 2015). The contrast between the bacterial abundance and organic substrate utilisation is an indication that bacterial abundance per se cannot explain substrate utilisation. In a recent work, Ziervogel et al. (2015)

found out that bacterial protein production (community activity) was lower in sediments than water despite higher hydrolytic activities in the sediments. They postulated that a portion of the hydrolytic enzymes required to break down organic substrates might already be present in the sediment attached to mineral particles. The role of extracellular enzymes has also been demonstrated by Münster et al. (1992).

The similar cell counts data before and after resuspension could also be due to bacterial stripping by resuspended particles. Guizien et al. (2014) did not observe bacteria enrichment in water after tidal sediment erosion and they attributed this to potential sorption of bacteria to mineral surfaces. Jiang et al. (2007) found out that adsorption of *Pseudomonas putida* to mineral surfaces followed the order goethite > kaolinite > montmorillonite. The striking difference in resuspension effects on cell counts in spring and summer could be an indication of a faster after resuspension acclimation of benthic heterotrophic organisms in spring than in summer.

What controls DOC after resuspension?

Immobilization of DOC can occur mainly due to degradation by bacteria or by adsorption to mineral surfaces e.g. Fe oxyhydroxides. Bacterial C consumption contributing to C immobilization after resuspension was observed in both Rote Mulde and Rappbode shallow sites. Thus, the DOC was probably partially converted to microbial biomass. Interestingly, our results also show that bacterial C consumption reduces C mobilization (Rappbode deep site) and that bacteria biomass contributes to C mobilization (Rappbode shallow site, June). The microbial immobilization of carbon diminished from March to June which could indicate potential change in DOC quality. Utilisation and competition for labile carbon sources is high in summer and this can lead to accumulation of more aromatic carbon substrates which are not easily utilisable for microorganisms. It is therefore clear that there is another immobilization pathway responsible for the observed reduction in DOC concentration.

The observed differences between resuspension effects under oxic and anoxic conditions can be explained by sorption of DOC to ferric minerals. In Hassel shallow site under oxic conditions Fe concentration increased after resuspension and DOC was immobilized, furthermore the mean DOC:Fe molar ratio decreased from around 200 to 100. In Rote Mulde the DOC immobilization was higher than in Hassel however Fe concentration decreased after resuspension and the DOC:Fe ratio decreased from 19 to 16. The high DOC:Fe in Hassel shallow site under oxic conditions indicates Fe limitation hence a limited adsorption capacity. Adsorption of DOC to Fe minerals has been demonstrated in many soil science studies (Chen et al. 2014; Guggenberger et al. 1998; Kalbitz et al. 2000) and aquatic studies (Mc Dowell 1985; Skoog and Arias-Esquivel 2009).

The adsorption mechanism which immobilizes DOC seemed to become weaker with repeated resuspension when water was not changed. Even though the effect apparently levelled off after 3 weeks of weekly resuspension without change of water, there is a possibility that in the natural system this might be countered by deposition of fresh organic and mineral particles. The increased DOC immobilization when resuspension was done after exchange of water could be due to higher sorption capacity of Fe minerals and organic carbon in the replacement water compared to the replaced water. It also indicates preferential absorption of DOC which could have exhausted the absorbable DOC during the initial resuspension with no water exchange. The decreasing DOC immobilization when water was not exchanged and the subsequent increase in DOC immobilization when water was exchanged confirms the typical adsorption of organic matter and phosphorus to Fe oxyhydroxides, which tends to saturate when all the adsorption sites on the iron minerals have been occupied.

The higher immobilization of DOC in Rote Mulde compared to Hassel and Rappbode pre-dams can be explained by the higher specific ultraviolet absorption at 254 nm ($SUVA_{254nm}$) which was 5, 3, and 4 L mg C^{-1} m^{-1} for Rote Mulde, Hassel and Rappbode respectively. According to Edzwald and Tobiason (1999) classification, SUVA between 2 and 4 L mg^{-1} C m^{-1} enables a DOC removal of 25-50% by alum coagulation while that > 4 L mg^{-1} C m^{-1} indicates removal of >50%. Specific ultraviolet absorption only slightly increased expectedly after resuspension under oxic conditions since the small volume of porewater introduced into the overlying water was diluted. The $SUVA_{254nm}$ was not used to interpret DOC quality under anoxic conditions because UV absorption is affected by dissolved Fe (Dadi et al. 2015). The low pH in Rote Mulde might have further contributed to the higher immobilization of DOC. Water pH has an effect on surface charge and ionic strength therefore it can alter adsorption properties of DOC (Gu et al. 1994; Tipping 1981). Several studies have demonstrated leaching of DOC with increasing pH (Andersson et al. 2000; Andersson et al. 1994; Evans et al. 2012; Kerr and Eimers 2012).

However, DOC does not only adsorb to iron minerals. The negative correlation between sediment organic matter content and the resuspension effect on DOC shows, that the benthic DOC dynamic was likely influenced by adsorption of DOC to organic particles. It is well known that DOC can adsorb to particulate organic carbon (POC) particles (Mc Dowell 1985). By this mechanism, a higher organic matter content in the sediment leads to a lower mobilisation of DOC upon resuspension.

Practical implications of resuspension

Resuspension has been long regarded as a problematic process in aquatic systems. This is not surprising considering that the focus has been on nutrients in shallow and nutrient rich systems. In this study we show that resuspension does not necessarily increase internal nutrient loading in nutrient poor systems.

However, resuspension affects carbon cycling by transferring benthic microorganisms into the water column. We also noted that resuspension had a long lasting effect by increasing the diffusive flux after particular resuspension events. This can be both beneficial and detrimental depending on the system and direction of the flux. In the case of Rote Mulde it promoted mobilization of Fe minerals from the sediment hence increased immobilization of DOC from the water column. However, in Fe limited systems increase in DOC will still be inevitable. Thus, in terms of DOC removal, resuspension can be beneficial in low nutrient – high iron systems. However, compared to other processes in the reservoirs carbon cycle (Dadi et al. 2016), the effect of resuspension has to be regarded as of minor importance. The stimulation of benthic resuspension, e.g. by introduction of benthivorous fish, is not a promising strategy to mitigate high DOC concentration in drinking water reservoirs.

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References

Andersson S, Nilsson SI, Saetre P (2000) Leaching of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in mor humus as affected by temperature and pH. Soil Biol and Biochem 32:1-10. doi:10.1016/S0038-0717(99)00103-0

Andersson S, Valeur I, Nilsson I (1994) Influence of lime on soil respiration, leaching of DOC, and C/S relationships in the mor humus of a haplic podsol. Environ Int 20:81-88. doi:10.1016/0160-4120(94)90070-1

Björnsen Beratende Ingenieure GmbH (2012) Fortschreibung der Potentialstudie für das Bodesystem Bestandsaufnahme (Updating the potential study for Bode System inventory). In German. Talsperrenbetrieb Sachsen-Anhalt: Anstalt des öffentlichen Rechts, Blankenburg, Koblenz

Bloesch J (1995) Mechanisms, measurement and importance of sediment resuspension in lakes. Mar and Freshwater Res 46:295-304. doi:10.1071/MF9950295

Carroll T, King S, Gray SR, Bolto BA, Booker NA (2000) The fouling of microfiltration membranes by NOM after coagulation treatment. Water Res 34:2861-2868. doi:10.1016/S0043-1354(00)00051-8

Chen C, Dynes JJ, Wang J, Sparks DL (2014) Properties of Fe-organic matter associations via coprecipitation versus adsorption. Environ Sci Technol 48:13751-13759. doi:10.1021/es503669u

Christian BW, Lind OT (2007) Multiple carbon substrate utilization by bacteria at the sediment-water interface: seasonal patterns in a stratified eutrophic reservoir Hydrobiologia 586:43-56. doi:10.1007/s10750-006-0476-6

Dadi T, Friese K, Wendt-Potthoff K, Koschorreck M (2016) Benthic dissolved organic carbon fluxes in a drinking water reservoir. Limnol Oceanogr 61: 445-459. doi:10.1002/lno.10224

Dadi T, Völkner C, Koschorreck M (2015) A sediment core incubation method to measure the flux of dissolved organic carbon between sediment and water. J Soil Sediment 15:2350-2358. doi:10.1007/s11368-015-1213-4

de Vicente I, Cruz-Pizarro L, Rueda FJ (2010) Sediment resuspension in two adjacent shallow coastal lakes: controlling factors and consequences on phosphate dynamics. Aquat Sci 72:21-31. doi:10.1007/s00027-009-0107-1

Edzwald JK, Tobiason JE (1999) Enhanced coagulation: US requirements and a broader view. Water Sci Technol 40:63-70. doi:10.1016/s0273-1223(99)00641-1

Eikebrokk B, Vogt RD, Liltved H (2004) NOM increase in Northern European source waters: Discussion of possible causes and impacts on coagulation/contact filtration processes Wa Sci Technol 4:47-54

Evans CD et al. (2012) Acidity controls on dissolved organic carbon mobility in organic soils. Global Change Biol 18:3317-3331 doi:10.1111/j.1365-2486.2012.02794.x

Evans CD, Monteith DT, Cooper DM (2005) Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. Environ Pollut 137:55-71. doi:10.1016/j.envpol.2004.12.031

Fischer J, Krogman R, Quist M (2013) Influences of native and non-native benthivorous fishes on aquatic ecosystem degradation. Hydrobiologia 711:187-199. doi:10.1007/s10750-013-1483-z

Garstecki T, Wickham SA, Arndt H (2002) Effects of experimental sediment resuspension on a coastal planktonic microbial food web. Estuar Coast Shelf S 55:751-762. doi:10.1006/ecss.2001.0937

Gibson B, Ptacek C, Blowes D, Daugherty S (2015) Sediment resuspension under variable geochemical conditions and implications for contaminant release. J Soil Sediment 15:1644-1656. doi:10.1007/s11368-015-1106-6

Goetz D, Kröger R, Miranda LE (2014) Effects of Smallmouth Buffalo, *Ictiobus bubalus* biomass on water transparency, nutrients, and productivity in shallow experimental ponds. Bull Environ Contam Toxicol 92:503-508. doi:10.1007/s00128-014-1231-8

Gough R, Holliman PJ, Heard TR, Freeman C (2014) Dissolved organic carbon and trihalomethane formation potential removal during coagulation of a typical UK upland water with alum, PAX-18 and

PIX-322. J Water Supply Res T 63:650-660. doi:10.2166/aqua.2014.007

Gu B, Schmitt J, Chen Z, Liang L, McCarthy JF (1994) Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models Environ Sci Technol 28:38-46. doi:10.1021/es00050a007

Guggenberger G, Kaiser K, Zech W (1998) Mobilization and immobilization of dissolved organic matter in forest soils. Z Pflanz Bodenkunde 161:401-408. doi: 10.1002/jpln.1998.3581610408

Guizien K, Dupuy C, Ory P, Montanie H, Hartmann H, Chatelain M, Karpytchev M (2014) Microorganism dynamics during a rising tide: Disentangling effects of resuspension and mixing with offshore waters above an intertidal mudflat. J Marine Syst 129:178-188. doi:10.1016/j.jmarsys.2013.05.010

Holmroos H, Hietanen S, Niemisto J, Horppila J (2012) Sediment resuspension and denitrification affect the nitrogen to phosphorus ratio of shallow lake waters. Fund Appl Limnol 180:193-205. doi:10.1127/1863-9135/2012/0223

Jiang D, Huang Q, Cai P, Rong X, Chen W (2007) Adsorption of Pseudomonas putida on clay minerals and iron oxide. Colloid Surface B 54:217-221. doi:10.1016/j.colsurfb.2006.10.030

Jones TG, Evans CD, Jones DL, Hill PW, Freeman C (2015) Transformations in DOC along a source to sea continuum; impacts of photo-degradation, biological processes and mixing. Aquat Sci :1-14. doi:10.1007/s00027-015-0461-0

Kalbitz K, Solinger S, Park JH, Michalzik B, Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: A review. Soil Sci 165:277-304 doi:10.1097/00010694-200004000-00001

Kerr JG, Eimers MC (2012) Decreasing soil water Ca^{2+} reduces DOC adsorption in mineral soils: Implications for long-term DOC trends in an upland forested catchment in southern Ontario, Canada. Sci Total Environ 427-428:298-307. doi:10.1016/j.scitotenv.2012.04.016

Koschinsky A, Gaye-Haake B, Arndt C, Maue G, Spitzy A, Winkler A, Halbach P (2001) Experiments on the influence of sediment disturbances on the biogeochemistry of the deep-sea environment. Deep-Sea Res Pt II 48:3629-3651 doi:10.1016/S0967-0645(01)00060-1

Laskov C, Herzog C, Lewandowski J, Hupfer M (2007) Miniaturized photometrical methods for the rapid analysis of phosphate, ammonium, ferrous iron, and sulfate in porewater of freshwater sediments. Limnol Oceanogr-Meth 5:63-71. doi:10.4319/lom.2007.5.63

Liang Y, Liu X, Xiao H, Gao X, Li W, Xiong J (2016) Impact of high water level fluctuations on stable isotopic signature of POM and source identification in a floodplain lake-Bang Lake (Poyang Lake). Environ Earth Sci 75:1-12 doi:10.1007/s12665-015-4847-z

Liikanen A, Martikainen PJ (2003) Effect of ammonium and oxygen on methane and nitrous oxide fluxes across sediment–water interface in a eutrophic lake. Chemosphere 52:1287-1293. doi:10.1016/S0045-6535(03)00224-8

Lovstedt CB, Bengtsson L (2008) The role of non-prevailing wind direction on resuspension and redistribution of sediments in a shallow lake. Aquat Sci 70:304-313. doi:10.1007/s00027-008-8047-8

Mc Dowell WM (1985) Kinetics and mechanisms of dissolved organic carbon retention in a headwater stream. Biogeochemistry 1:329-352. doi:10.1007/BF02187376

Meijer ML et al. (1994) Long-term responses to fish-stock reduction in small shallow lakes: interpretation of five-year results of four biomanipulation cases in The Netherlands and Denmark. Hydrobiologia 275-276:457-466. doi:10.1007/BF00026734

Morgan B, Rate AW, Burton ED (2012) Water chemistry and nutrient release during the resuspension of FeS-rich sediments in a eutrophic estuarine system. Sci Total Environ 432:47-56. doi:10.1016/j.scitotenv.2012.05.065

Müller S, Mitrovic S, Baldwin D (2015) Oxygen and dissolved organic carbon control release of N, P and Fe from the sediments of a shallow, polymictic lake. J Soil Sediment :1-12 doi:10.1007/s11368-015-1298-9

Münster U, Einiö P, Nurminen J, Overbeck J (1992) Extracellular enzymes in a polyhumic lake: Important regulators in detritus processing. Hydrobiologia 229:225-238 doi:10.1007/BF00007002

Niemisto J, Holmroos H, Pekcan-Hekim Z, Horppila J (2008) Interactions between sediment resuspension and sediment quality decrease the TN : TP ratio in a shallow lake Limnol Oceanogr 53:2407-2415. doi:10.4319/lo.2008.53.6.2407

Niemistö J, Tamminen P, Ekholm P, Horppila J (2012) Sediment resuspension: rescue or downfall of a thermally stratified eutrophic lake? Hydrobiologia 686:267-276. doi:10.1007/s10750-012-1021-4

Nowlin WH, Evarts JL, Vanni MJ (2005) Release rates and potential fates of nitrogen and phosphorus from sediments in a eutrophic reservoir. Freshwater Biol 50:301-322

Reddy KR, Fisher MM, Ivanoff D (1996) Resuspension and diffusive flux of nitrogen and phosphorus in a hypereutrophic lake. J Environ Qual 25:363-371. doi: 10.2134/jeq1996.00472425002500020022x

Ritzrau W, Graf G (1992) Increase of microbial biomass in the benthic turbidity zone of Kiel Bight after resuspension by a storm event. Limnol Oceanogr 37:1081-1086.doi: 0.4319/lo.1992.37.5.1081

Roberts J, Chick A, Oswald L, Thompson P (1995) Effect of carp, *Cyprinus carpio L*, an exotic benthivorous fish, on aquatic plants and water quality in experimental ponds. Mar Freshwater Res 46:1171-1180. doi:10.1071/mf9951171

Rožić M, Cerjan-Stefanović Š, Kurajica S, Vančina V, Hodžić E (2000) Ammoniacal nitrogen removal from water by treatment with clays and zeolites. Water Res 34:3675-3681. doi:10.1016/S0043-1354(00)00113-5

Saad OALO, Conrad R (1993) Temperature dependence of nitrification, denitrification, and turnover of nitric oxide in different soils. Biol Fert Soils 15:21-27. doi:10.1007/bf00336283

Scheffer M, Portielje R, Zambrano L (2003) Fish facilitate wave resuspension of sediment Limnol Oceanogr 48:1920-1926. doi:10.4319/lo.2003.48.5.1920

Simon M, Azam F (1989) Protein content and protein synthesis rates of planktonic marine bacteria. Mar Ecol-Prog Ser 51:201-213. doi:10.3354/meps051201

Skoog AC, Arias-Esquivel VA (2009) The effect of induced anoxia and reoxygenation on benthic fluxes of organic carbon, phosphate, iron, and manganese. Sci Tot Environ 407:6085-6092. doi:10.1016/j.scitotenv.2009.08.030

Søndergaard M, Jeppesen E, Mortensen E, Dall E, Kristensen P, Sortkjær O (1990) Phytoplankton biomass reduction after planktivorous fish reduction in a shallow, eutrophic lake: a combined effect of reduced internal P-loading and increased zooplankton grazing. Hydrobiologia 200-201:229-240. doi:10.1007/BF02530342

Søndergaard M, Kristensen P, Jeppesen E (1992) Phosphorus release from resuspended sediment in the shallow and wind-exposed Lake Arresø, Denmark. Hydrobiologia 228:91-99. doi:10.1007/BF00006480

Søndergaard M, Liboriussen L, Pedersen A, Jeppesen E (2008) Lake restoration by fish removal: short- and long-term effects in 36 Danish lakes. Ecosystems 11:1291-1305. doi:10.1007/s10021-008-9193-5

Stumm W, Morgen JJ (1996) Aquatic chemistry: Chemical equilibria and rates in natural waters. Third edn., New York

Tammeorg O, Niemisto J, Mols T, Laugaste R, Panksep K, Kangur K (2013) Wind-induced sediment resuspension as a potential factor sustaining eutrophication in large and shallow Lake Peipsi. Aquat Sci 75:559-570. doi:10.1007/s00027-013-0300-0

Tengberg A, Almroth E, Hall P (2003) Resuspension and its effects on organic carbon recycling and nutrient exchange in coastal sediments: in situ measurements using new experimental technology. J Exp Mar Biol Ecol 285-286:119-142. doi:10.1016/S0022-0981(02)00523-3

Tipping E (1981) The adsorption of aquatic humic substances by iron oxides. Geochim Cosmochim Ac 45:191-199. doi:10.1016/0016-7037(81)90162-9

Wainright SC (1990) Sediment-to-water fluxes of particulate material and microbes by resuspension and their contribution to the planktonic food web. Mar Ecol-Prog Ser 62:271-281. doi:10.3354/meps062271

Wendt-Potthoff K, Kloß C, Schultze M, Koschorreck M (2014) Anaerobic metabolism of two hydro-morphological similar pre-dams under contrasting nutrient loading (Rappbode Reservoir System, Germany). Int Rev Hydrobiol 99:350-362. doi:10.1002/iroh.201301673

Wobus A, Bleul C, Maassen S, Scheerer C, Schuppler M, Jacobs E, Röske I (2003) Microbial diversity and functional characterization of sediments from reservoirs of different trophic state. FEMS Microbiol Ecol 46:331-347. doi:10.1016/S0168-6496(03)00249-6

Ziervogel K et al. (2015) Enhanced particle fluxes and heterotrophic bacterial activities in Gulf of Mexico bottom waters following storm-induced sediment resuspension Deep-Sea Res Pt II (in press) doi:10.1016/j.dsr2.2015.06.017

Chapter 6: Dissolved organic carbon quality in drinking water reservoirs

Photo: Rappbode pre-dam wall showing deep sampling point (group of buoys on the left). Photo by Tallent Dadi

6.1 Overview

In this chapter I present DOC quality analysis. General DOC quality analysis for all pre-dams was done using $SUVA_{254\ nm}$ to determine aromaticity and hydrophobicity. To answer the question on whether benthic processes affect the DOC quality in the overlying water molecular DOC signatures were analysed for the Rappbode pre-dam using the FTICR-MS method (Chapter 2). This experiment was unique because in addition to the normal *in situ* conditions incubation it had a second incubation step under manipulated redox conditions. The DOC quality samples were taken to determine if DOC quality changed during the incubation and when redox conditions were manipulated. *In situ* vertical depth samples (including porewater) at the shallow and deep site were also taken and analysed for DOC quality using the FTICR-MS method.

6.2 Abstract

The general DOC quality in all pre-dams was analysed by SUVA $_{254\ \mathrm{nm}}$ during the sediment incubations. The effects of benthic processes on DOC quality in the overlying water were checked only in Rappbode pre-dam, through analysis of *in situ* vertical water and porewater samples, and samples derived from sediment incubation under different redox conditions, and redox conditions manipulation, by using the FTICR-MS method. Rote Mulde was found to have the highest SUVA $_{254\ \mathrm{nm}}$ values, while Hassel and Rappbode had lower SUVA $_{254\ \mathrm{nm}}$ values to those of Rote Mulde. This indicates that Rote Mulde is more aromatic and hence has a higher disinfection by-product formation potential compared to the other pre-dams. Benthic processes were shown to affect the DOC quality in the overlying water, with the hypolimnion at the stratified deep site showing a different DOC signature to that of the epilimnion. Redox conditions were found to have an effect on DOC quality, with release of oxygen rich compounds (which have a tendency to adsorb to Fe minerals) under anoxia but not under oxic conditions. This emphasise the preferential adsorption of certain DOC components to Fe minerals and the persistence of DOC compounds that cannot be adsorbed. The non-adsorbed compounds will therefore reach the water treatment plants and cannot be removed by coagulation methods prompting a further step to remove these compounds. The findings also indicate the potential preservation and burial of the oxygen rich compounds in the reservoirs.

6.3 Introduction

The DOC in a lake system is composed of both allochthonous and autochthonous DOC. Autochthonous DOC consists of protein, low-molecular-weight molecules from algae, aquatic macrophytes, and bacteria (Bertilsson and Jones Jr 2003) Allochthonous DOC includes aromatic, humic-like molecules from decomposition, and leaching terrestrial plant and soil derived organic matter (Mcknight et al. 2003). The ratio of these two depends on the amount of DOC imported from the catchment and also the productivity of a lake. In general allochthonous DOC is bound to dominate mainly because of huge amounts imported from the catchment and also because it’s more recalcitrant compared to the autochthonous (Lind 2002). Lake DOC signatures are expected to be changing from time to time because of the different processes e.g. DOC consumption and production.

These changes are due to the loss of DOM functional groups. Kothawala et al. (2012a) found that carboxyl groups are lost first, followed by aromatic groups and then other functional groups and they also found a shift from higher to lower molecular weight DOC. There is heterogeneity in occurrence and magnitude of these processes within lake systems. Therefore inflow points in lakes with a longer retention times are expected to have different DOC signatures compared to the outflow points. Drivers like redox conditions and temperature also influence the DOC production and consumption processes. In their study, Riedel et al. (2013) found that Fe traps DOC at redox interfaces, a mechanism which can change the DOC signatures. The sediment water interface is a redox conditions interface hence it was interesting to find out if there were changes in DOC quality during the incubation and also to determine if redox condition manipulations had influence in DOC quality.

The research questions were, does: 1) $SUVA_{254\ nm}$ differ among the pre-dams, 2) the DOC coming out of the sediment have a different quality from that in the overlying water, and if this result in vertical gradient of DOC quality in the water column, and 3) redox conditions manipulations result in change in DOC quality. The objectives to answer these questions were to:

i. Determine the $SUVA_{254\ nm}$ in all pre-dams
ii. Determine depth profile DOC quality in riverine and profundal zones of a pre-dam.
iii. Determine effects of sediment incubation and redox conditions manipulation on DOC quality.

6.4 Methods

6.4.1 Specific ultraviolet absorption ($SUVA_{254\ nm}$)

Ultraviolet absorbance at 254 nm was analysed for all the sediment core incubations samples from the three pre-dams. Details about when the sediment incubation were done in each pre-dam have been described in Chapter 4b. The samples (1 ml) were filtered using a GFF filter and analysed photometrically (DIN_38404-3:2005-07 2005) in a quartz cuvette (Hach Lange DR 500; Hach Lange, Germany). The $SUVA_{254\ nm}$ was calculated by dividing ultraviolet absorbance at 254 nm by the respective DOC concentration for each sample. Methods for the DOC concentration determination are described in Chapter 2, 3 and 4a.

6.4.2 Analysis of DOC quality

Analysis of DOC quality experiment was only carried out for Rappbode in September 2014 and was coupled to the Rappbode September 2014 sediment core incubation. This incubation included a second incubation step after the normal *in situ* incubation. The second incubation step was done after manipulation of the redox conditions in the sediment cores i.e. from oxic to anoxic for the shallow site, and from anoxic to oxic for the deep site.

The aim of this experiment was to investigate whether there are: 1) spatial (vertical and horizontal) DOC quality gradients within a drinking water reservoir pre-dam, and 2) DOC quality changes during incubation period and after manipulation of redox conditions. This was achieved by taking vertical (including porewater) samples in the Rappbode pre-dams and samples at different times of the sediment incubation period.

Surface and bottom water samples were taken from both shallow and deep sites using a standard 2-l water sampler (Hydrobios, Kiel, Germany). An additional sample was taken for the deep site at 3.5 m, which was the depth of the oxycline. Six sediment cores (9 cm in diameter) were sampled from each site using a gravity corer (UWITEC, Mondsee, Austria); two sediment cores for sediment porewater extraction and four cores for sediment incubation. The upper 3 cm sediment layer of the two sediment porewater cores were sectioned on site and combined into one sample. Part of the mixed sample was used for porewater extraction and the other part was used for sediment quality analysis i.e. water content and loss on ignition. Porewater was extracted by centrifugation at 3750 rpm for 15 minutes at the incubation temperature.

Four sediment cores were incubated at *in situ* conditions for 12 days after which redox conditions were manipulated/switched and the sediment cores were incubated again for another 15 days. The sediment incubation procedure is described in detail in Chapter 4a. The cores were initially incubated at *in situ* redox conditions and temperature (oxic, 14^{o}C for shallow and anoxic 6^{o}C, for deep) for 13 days. The cores were then incubated at manipulated redox conditions and *in situ* temperature (anoxic, 14^{o}C for shallow and oxic, 6^{o}C for deep) for 14 days. During the sediment incubation 30 ml water samples were taken every 3 days and analysed for DOC, UV254$_{nm}$, TIC, CH_4, NH_4^+ , NO_3^- , SRP, SO_4^{2-} , Fe, and Mn using methods described in Chapter 2. Samples volume was replaced with bottom water samples. Controls were prepared by incubating bottom water samples at *in situ* temperature and redox conditions. Three DOC quality samples (combined from the four cores) were taken from each site; 1) at the start of the *in situ* redox condition incubation, 2) before redox manipulation, and 3) at the end of the manipulated redox condition incubation. Altogether there were 13 samples analysed for DOC quality (7 depth samples and 6 incubation samples). All DOC quality samples were analysed by FTICR-MS method described in chapter 2.

6.5 Results

6.5.1 Specific ultraviolet absorption (SUVA$_{254\ nm}$)

The lowest SUVA$_{254\ nm}$ values were observed in Hassel shallow sites with Rote Mulde having the highest among the shallow sites (Table 6.1). Hassel and Rappbode deep sites SUVA is comparable under anoxic conditions, while the Rappbode deep site SUVA under oxic conditions is comparable to that of Rappbode shallow site. From the results of DOC and Fe concentrations in the overlying water during sediment incubation (Chapter 4b), I calculated the DOC:Fe molar ratios. The DOC:Fe molar ratios were higher in the Hassel and Rappbode shallow sites and lower in the Rote Mulde, which is also a shallow site (Table 6.1). The deep site DOC:Fe ratio for Hassel and Rappbode is very similar and was lower than that of the shallow sites both under oxic and anoxic conditions. However the oxic deep sites ratio was higher compared to the anoxic ratio.

Table 6.1: Mean molar DOC:Fe concentration ratio and $SUVA_{254\ nm}$ in overlying water during sediment incubation. Values in brackets are under anoxic conditions. Note, [a] n = 5, [b] n = 4, and [c] n = 3.

	Hassel		**Rappbode**		**Rote Mulde**
	shallow	**deep**	**shallow**	**deep**	
DOC:Fe molar ratio	222 ± 69[a]	14 (2 ± 1)[b]	97 ± 118[c]	14 (4)	35 ± 25[c]
$SUVA_{254nm}$ [L mg^{-1} C m^{-1}]	3.3 ± 0.3[a]	(14.1 ± 1.3)[a]	4.1 ± 0.7[a]	5 ± 1[c] (10 ± 5)[c]	5.4 ± 0.3[a]

6.5.2 Redox conditions manipulation

During the initial incubation step, cores incubated under oxic conditions (shallow site) immobilized DOC and those incubated under anoxia (deep site) released DOC (Fig. 6.1). Similarly, when redox conditions were manipulated, DOC flux direction also changed. The influence of redox conditions is also seen in other solutes as well (Fig. 6.1).

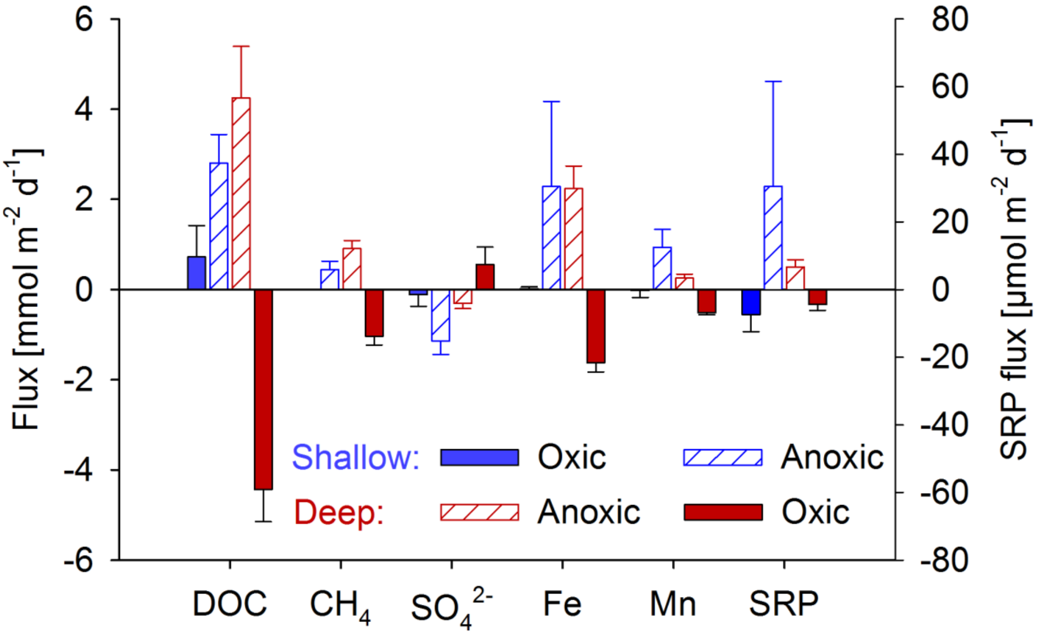

Fig. 6.1. Solute fluxes for Rappbode shallow and deep site sediments incubated first at *in situ* redox conditions followed by a redox conditions manipulation. The shallow and deep sediments were oxic and anoxic respectively at in situ conditions. Error bars represent standard deviation of four replicates cores.

6.5.3 Cluster analysis of DOC quality samples

The DOC quality at different water layers, and redox conditions in Rappbode pre-dam was compared by a cluster analysis. Intensity ranking pattern of carbon, hydrogen, and oxygen (CHO) components which were present in all 13 water samples analysed (Fig 6.2). Quality of DOC was quite similar in all samples from the epilimnion (shallow 0 m, 3.8 m, deep 0 m, and 3.5 m). The deep 15 m (hypolimnion) sample was somewhat different from the epilimnion samples. Porewater samples from both shallow and deep sites were quite different from all other pelagial samples and also quite different from each other. The deep anoxic incubation start sample was similar to the deep 15 m as expected. This water was used for incubation of the sediment. Analogous to that, the shallow oxic incubation start sample was similar to the shallow 3.8 m samples and all other epilimnion samples. The deep anoxic incubation end sample was similar to the deep porewater sample, but quite different from all other samples. Shallow oxic incubation end sample was similar to the shallow pore water sample and different from all the other samples. The redox conditions manipulation from oxic to anoxic at the deep site resulted in similarity to that at the anoxic incubation start and the hypolimnion water (15 m). At the shallow site, the redox conditions manipulations from oxic to anoxic resulted in a similarity to the oxic incubation start sample. However the oxic incubation start sample was quite different from the oxic incubation end sample. The differences in samples for both shallow and deep site, when comparing the start of incubation and the samples after redox condition manipulations were more pronounced at the shallow site.

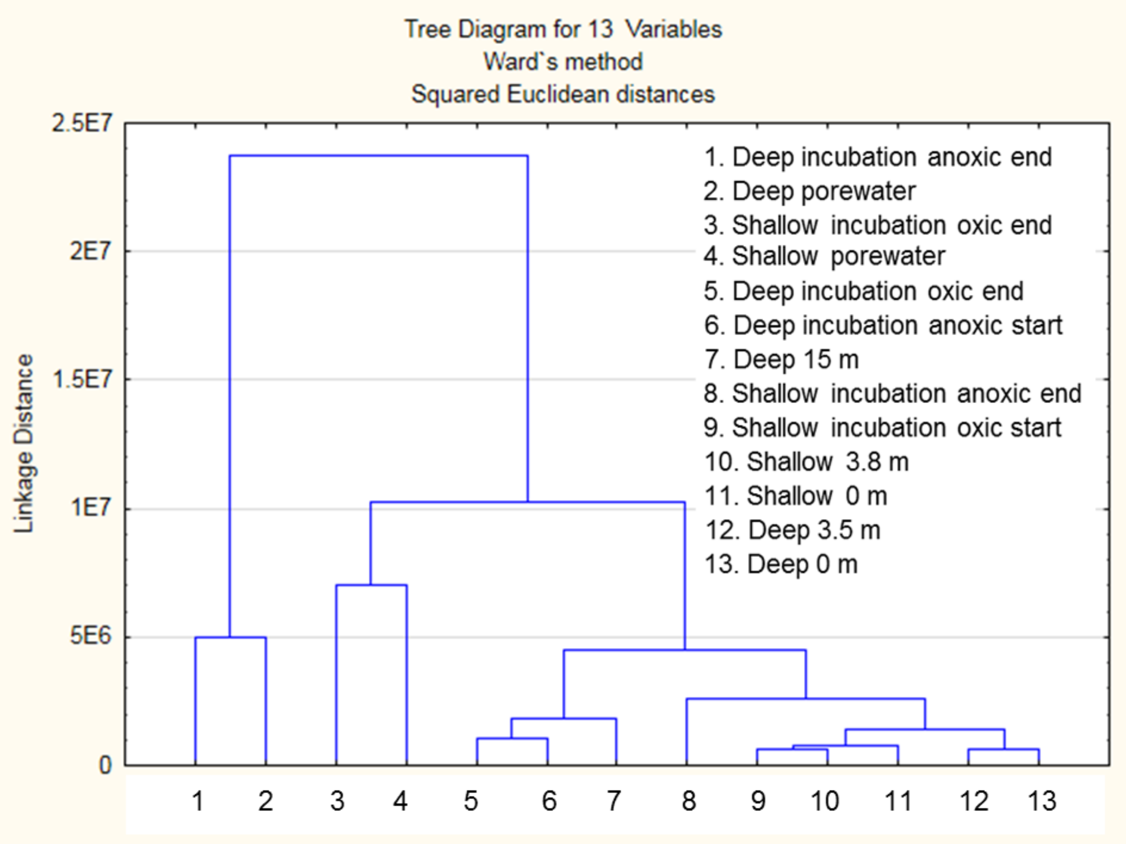

Fig. 6.2. Cluster analysis of CHO components of vertical depth samples and sediment incubation samples from Rappbode shallow and deep sites.

6.5.4 Inter sample ranking analysis of DOC quality samples

The DOC quality of samples was also distinguished by inter sample ranking analysis (Herzsprung et al. 2012a). As seen from cluster analysis the deep epilimnion samples (0 m and 3.5 m were quite similar to each other (Fig. 6.3). The deep hypolimnion sample (15 m) showed relative high intensities (first ranks) in the region $1 < \text{hydrogen/carbon ratio (H/C)} < 1.5$ and oxygen/carbon ratio (O/C) < 0.6. Relative low intensities (last/fourth ranks) could be observed for $H/C < 1$ and $O/C > 0.6$. The deep pore water sample showed opposite (to deep 15 m) ranking of intensities. First ranks were found for oxygen rich and relatively unsaturated (tannin-like) components with $H/C < 1$ and $O/C > 0.6$ and in addition for many components with $H/C < 1$ and $0.4 < O/C < 0.6$. Many components with $O/C > 0.5$ and $1 < H/C < 1.3$ showed first and second ranks in the pore water sample. Components with $1 < H/C < 1.5$ and $O/C < 0.5$

mainly showed last ranks (fourth ranks). Some higher saturated components with $H/C > 1.5$ showed first ranks in the pore water sample. In summary the pore water was dominated by oxygen rich and relative unsaturated tannin-like components and some more aliphatic (lipid-like) components. The deep hypolimnion water (15 m) was dominated by less oxygen rich lignin like components. The deep epilimnion water showed intermediate DOC quality compared to the pore water and the deep hypolimnion water.

Comparing the three samples from shallow site, the pore water as the most different showed first ranks for components with $O/C > 0.5$ and $1 < H/C < 1.5$, for components with $O/C < 0.6$ and $0.5 < H/C < 1.0$ and some lipid like components with $H/C > 1.4$. Both many (but not all of them) lignin-like components with $1 < H/C < 1.5$ and $O/C < 0.5$ and tannin-like components with $H/C < 1$ and $O/C > 0.6$ showed relative low intensities (last / third) ranks in the shallow pore water sample compared to the corresponding shallow epilimnion water samples (Fig 6.3).

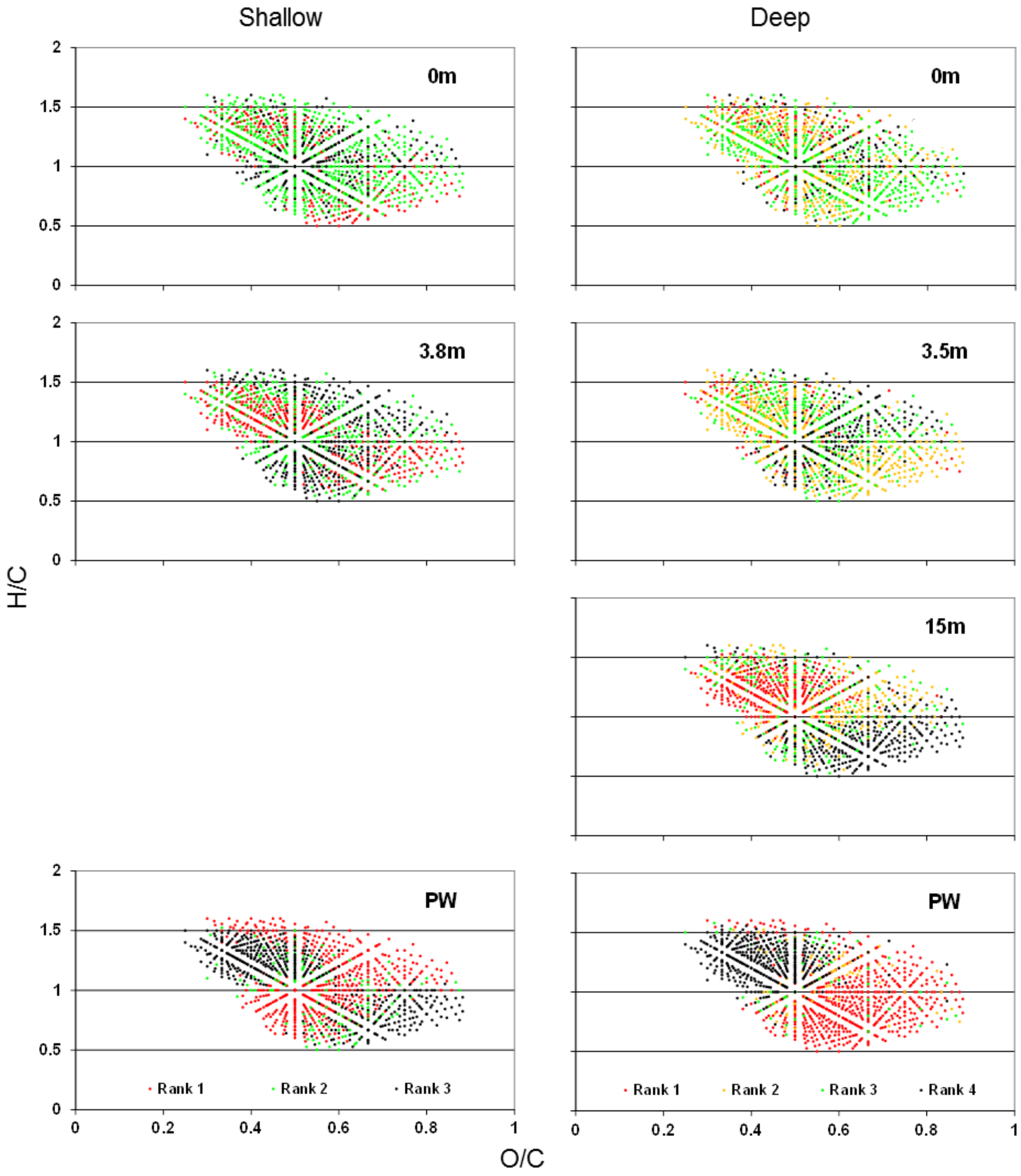

Fig. 6.3. Van Krevelen's diagrams showing inter samples ranking analysis of DOC quality of the vertical depth samples (epilimnion, hypolimnion and porewater) and sediment incubation samples from Rappbode shallow (left) and deep (right) sites.

The incubation experiments showed DOC quality change. At the deep site, anoxic incubation of sediment cores changed the intensity ranking dramatically as shown by the anoxic start and end of the incubation. (Fig. 6.4). Oxygen rich components now showed first ranks and oxygen poor components third (last) ranks. After the redox conditions manipulation from anoxic to oxic the DOC quality changed nearly to the initial status at the start of the anoxic incubation, a result similar to that shown by the cluster analysis. At the shallow site the sediment cores were initially incubated under oxic conditions. The oxygen rich components showed last ranks whereas oxygen poor components showed first ranks (Fig 6.4). The redox conditions manipulation from oxic to anoxic again changed DOC quality at the shallow site. At the end of the oxic incubation, at the shallow site, the sample showed now first ranks for oxygen rich components and third ranks for oxygen poor components.

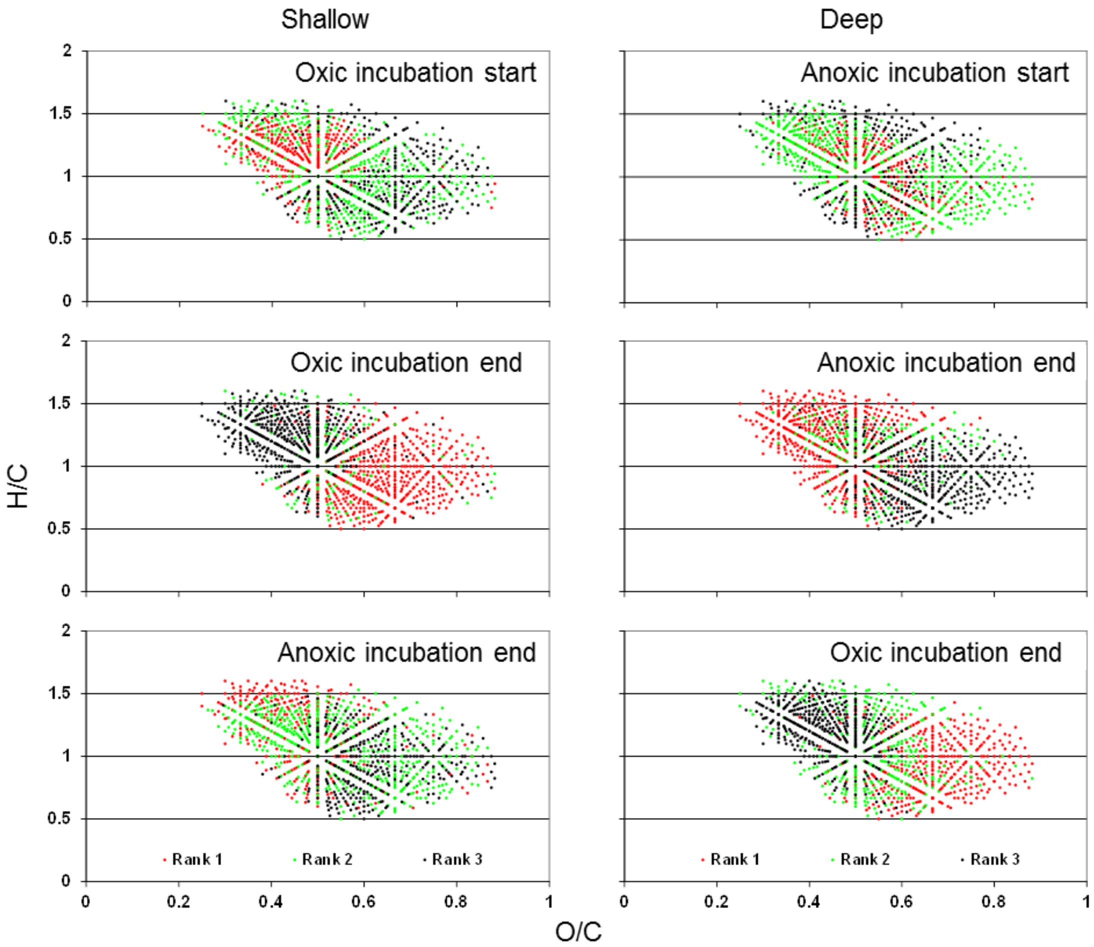

Fig. 6.4. Van Krevelen's diagrams showing the inter samples ranking analysis of DOC quality of *in situ* redox (upper 2 charts) and manipulated redox conditions (bottom chart) sediment incubation samples from Rappbode shallow (left) and deep (right) sites.

To better compare the shallow and deep site sediment incubations a new inter sample rankings analysis (Fig 6.5) was performed considering only the before redox manipulation (shallow oxic incubation end, deep anoxic incubation end) and the after redox conditions manipulation (shallow anoxic incubation end, deep oxic incubation end). Anoxic incubation led to relative higher intensities for the highest oxygenated components with O/C > 0.8 at the shallow site. At the deep site anoxic incubation showed finally the highest intensities for components with 0.5 < O/C < 0.8. Oxic incubation showed lower relative intensities of oxygen rich components in shallow site compared to deep site.

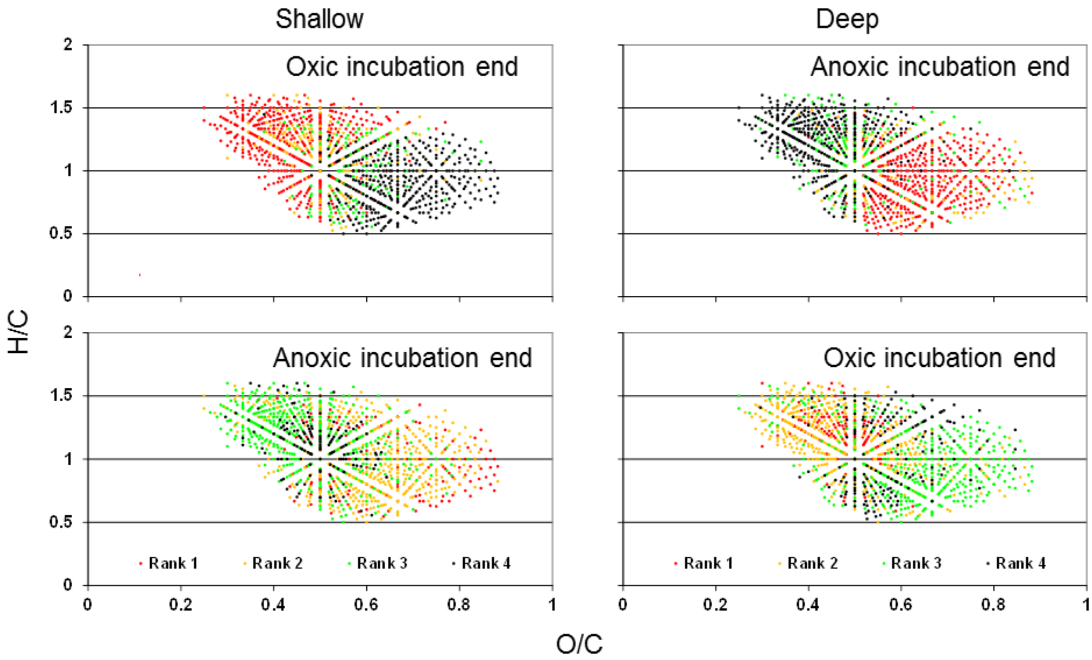

Fig. 6.5. Van Krevelen's diagrams showing the inter samples ranking analysis of DOC quality at the end of *in situ* redox (upper) and end of manipulated redox conditions (bottom) sediment incubation samples from Rappbode shallow (left) and deep (right) sites.

6.6 Discussion

The DOC quality experiments were carried out for two purposes. The first was to determine if DOC quality varied with vertical depth profiles (from overlying water to porewater) of the shallow and deep site, and if there were DOM quality differences in the epilimnion of the shallow and deep site. The second was to determine if DOC quality changed during sediment incubation and when redox conditions were manipulated.

6.6.1 Aromaticity of DOC in the pre-dams

Aromaticity of DOC is important because it affects DOC reactivity, more aromatic DOC is less biodegradable (Kalbitz et al. 2003; Saadi et al. 2006). Aromaticity of DOC is positively correlated with $SUVA_{254\ nm}$ and hydrophobicity (Chin et al. 1994; Weishaar et al. 2003), and can be used to determine DOC quantity and quality (Carter et al. 2012). Hassel had the least aromatic DOC while Rote Mulde has the most aromatic DOM. The lower aromaticity of DOC in Hassel than Rappbode agrees with the finding of Tittel et al. (2015), which shows (based carbon isotope composition) that DOC in the Hassel catchment is younger than that from the Rappbode catchment. The $SUVA_{254\ nm}$ values for the deep sites were very high, indicating Fe interference (Weishaar et al. 2003; Fellman et al. 2010; Sleighter et al. 2015). Rote Mulde had the lowest DOC:Fe ratio among the shallow sites, which is in agreement with the higher immobilization of DOC in Rote Mulde (Chapter 4b). Lower DOC:Fe ratio indicates availability of sorption sites while higher DOC:Fe ratio indicates limitation of sorption sites for DOC. The deep sites even had a lower DOC:Fe ratio, which indicates that they have a greater potential to immobilize DOC when they are exposed to oxic conditions. From the $SUVA_{254nm}$ and DOC:Fe ratios it can be clearly seen that Rote Mulde is different compared to Hassel and Rappbode, in terms of DOC quality, and potential for DOC adsorption to Fe minerals. Disinfection by-products (DBP) formation potential during water treatment is known to be positively correlated to SUVA$_{254\ \mathrm{nm}}$, however other DBP do not absorb at 254 nm (Weishaar et al. 2003). Therefore the SUVA$_{254\ \mathrm{nm}}$ results could imply a higher DBP formation potential in Rote Mulde compared to the other pre-dams. However, DBP formation potential is also triggered by algae, therefore eutrophic reservoirs with lower SUVA$_{254\ \mathrm{nm}}$ values may also have a high DBP formation potential.

6.6.2 Vertical and horizontal DOC quality gradients

This section answers the question whether benthic processes affect vertical and horizontal DOC quality gradients. At the shallow site there was no vertical DOC quality gradient in the overlying water (0 m, and 3.5 m), which indicates the dilution effects on the DOC mobilized from the porewater. Vertical DOC quality gradients were observed at the deep site, where the epilimnion DOC quality was totally different from that in the hypolimnion. This indicates the accumulation of DOC mobilized from the porewater and also the difference in the redox condition between the epilimnion and hypolimnion.

The differences in DOC quality in the shallow and deep site epilimnion (horizontal gradient) was negligible indicating that there is relatively small change in DOC quality as water moves from the inflow (shallow site) to the outflow (deep site). The Rappbode pre-dam, which was sampled for the DOC quality analysis, has a mean water residence time of 52 days (Friese et al. 2014). Morling et al. (2016) measured DOC degradation in Rappbode epilimnetic water and found a degradation of 13-20% over a period of 91-131 days, which indicates that DOC reaching the outflow in the reservoir is still dominated by allochthonous DOC from the catchment. In their study

Friese et al. (2014) found out that the water in Rappbode was more aromatic compared to Hassel, therefore this water is dominated by allochthonous DOC. The results of this study are in agreement with the observed long-time required to transform DOC (Middelburg 1989; Catalan et al. 2016).

6.6.3 Redox conditions affects DOC

The DOC quality analysis was also done to find out if the DOC mobilized from the sediment has a different signature to that in the overlying water, and to determine the effects of redox conditions on DOC quality. Redox conditions influenced DOC quality. The results demonstrate that anoxic conditions promote a release of oxygen rich DOC components. These components are rich in carboxyl groups and therefore are adsorbed to ferric iron minerals (Gu et al. 1994). If ferric iron is reduced to ferrous iron, such DOC components are no longer adsorbed. Oxic conditions promote iron precipitation. Oxygen rich organic components are then co-precipitated with iron minerals. This result concurs with the concurrent release of DOC and Fe under anoxic conditions and concurrent immobilization under oxic conditions (Fig. 6.1). In another study in Rote Mulde River, which is the feeding stream to Rote Mulde pre-dam, Herzsprung et al. (2012a) found out that oxygen rich compounds were present in July but not in March. They attributed this to potential leaching of oxygen rich compounds from the catchment. It therefore indicates anoxia in catchment soils probably due to increased temperatures in summer and subsequent leaching of these compounds into the streams.

Interestingly the porewater DOC quality of both deep and shallow site was different to that at the start of incubation but very similar to DOC quality at the end of *in situ* incubation. This strongly depicts the DOC fluxes, which were observed during this period. The deep site was anoxic; however the deep site pore water contained relatively higher amounts of oxygen rich organic components than the hypolimnion water (15 m). This probably indicates the stripping of oxygen rich DOC components by ferric iron prior to anoxia. This leads to the observed elevated oxygen rich DOC components in anoxic porewater after the reduction of ferric iron. In contrast to the deep site, the shallow pore water (upper 1 cm) was oxic. Therefore the oxygen rich components are adsorbed to iron minerals hence a lower signal of these compounds.

Anoxic sediments are a temporary source for ferrous iron and oxygen rich components, both which can be precipitated at the oxic/anoxic boundary. This is a relevant process during the autumn lake overturn when the anoxic hypolimnetic water mixes with the oxic epilimnetic water. If the sediment is oxic, it is a temporary sink of iron and oxygen rich components. The DOC quality results strongly show that DOC quality change due to microbial degradation is minimal however redox conditions have a strong impact on DOC quality. This is interesting especially at redox condition boundaries where microbial decomposition of DOC might be constrained because of immobilization of oxygen rich DOC components by Fe minerals. The findings on oxygen rich compounds further emphasize the preferential adsorption on oxygen rich compounds. This promotes burial and preservation of carbon (Lalonde et al. 2012) and persistence of aliphatic compounds (Kellerman et al. 2015). For drinking water treatment this implies that coagulation alone is not enough to remove the DOM since the aliphatic compounds cannot be removed by this method (Cortés-Francisco et al. 2014).

Chapter 7: Overall discussion

7.1 Overview

This chapter brings together the major findings of this thesis, which have been discussed in the preceding chapters (3 to 6). The main results of this thesis are highlighted in italics. I also look at implications of the findings and highlight research gaps emanating from the findings.

7.2 Sediment incubation method

A method to measure DOC fluxes at the sediment water interface under both oxic and anoxic conditions was developed. Most important was that the method addressed the most crucial aspects of mimicking *in situ* conditions: stirring of overlying water immediately after sampling, transportation of sediment cores in insulated boxes, sediment incubation at *in situ* temperatures and redox conditions. Sediment incubation has been done in many ways before. The method incorporated all crucial aspects of sediment core incubations and I am confident that it could be a strong initiative in contributing to a standardized sediment incubation method in the future.

It is important that care is taken to separate fast fluxes from slow fluxes. For example solutes like oxygen have a high flux and should be determined right at the start of the experiment i.e. up to 1 day, while solutes with slow fluxes like DOC should be measured over a longer period i.e. up to 14 days. The duration of incubation depends on the flux magnitude, and analytical limits. The duration of incubation should be kept minimal to minimise the influence of *in situ* condition that normally would change in the long term but cannot be mimicked in the set up e.g. sedimentation of fresh particles. Another reason is to prevent depletion of nitrate, which can occur in long time incubations. It is therefore anticipated that in highly eutrophic systems incubation could be shorter than 14 days because fluxes are expected to be high in these systems.

It has become evident that presence of bubbles in sediment incubation core interferes with oxygen measurements in oxic cores. Bubbles can carry high amount of oxygen, which when it dissolve in water increases oxygen concentration leading to errors in determination of oxygen consumption rates. It is therefore imperative that all bubbles are removed prior to start of oxygen flux measurements. To make this task much more efficient it is recommended, to modify the sediment stirrers design by incorporating a sloping inside surface such that the 20 mm diameter opening (refer to Chapter 3, Fig. 1) in the setup is sitting on the upper end of this slope. This would allow all bubbles to slide to the opening leaving no bubble trapped inside the core.

It has been found out that DOC:$UV_{254\ nm}$ *correlation is site specific. The correlations were strong and significant under oxic conditions and weak under anoxic conditions, therefore* $UV_{254\ nm}$ *is not a good proxy of DOC under anoxic conditions.* This could have been due to interference of Fe (Weishaar et al. 2003; Poulin et al. 2014), since Fe exists in the dissolved ferrous state under anoxic conditions. Nitrate also interferes with $UV_{254\ nm}$ (Weishaar et al. 2003), however under anoxic conditions there was no nitrate in the samples. Davis et al. (2001) found a close positive correlation between Fe and UV_{254nm} and they attributed it to silica mobilization of Fe colloids. This proxy is widely used to determine DOC concentrations and therefore it’s important to know the redox conditions in the water at the time of measurements to ensure that the proxy is used only under oxic conditions.

7.3 Direction and magnitude of the DOC flux

Mean sediment incubation oxic DOC fluxes for Hassel, Rappbode and Rote Mulde pre-dams were -0.01, -0.75, and -3.65 mmol m^{-2} d^{-1} respectively, while the anoxic DOC fluxes for Hassel and Rappbode were 1.56 and 3.56 mmol m^{-2} d^{-1} respectively. In comparison the estimated DOC fluxes (turnover rates) from hypolimnion inventories for Hassel and Rappbode were 0.5 and 1.6 mmol m^{-2} d^{-1} respectively (Chapter 2). *The anoxic sediment incubation and hypolimnion turnover rates are within the same order of magnitude, which indicates plausibility of the sediment incubation method developed and used in this thesis.* The differences in the sediment incubation and hypolimnion inventories DOC fluxes could be an indication of DOC consumption in the hypolimnion; hence the lower hypolimnion inventories DOC fluxes. Oxic DOC fluxes are within the same order of magnitude to what has been reported in the literature (Burdige and Homstead 1994; Gale and Reddy 1994; Demarty and Prairie 2009; Skoog and Arias-Esquivel 2009; Zheng et al. 2011; Yang et al. 2014).

The DOC flux data clearly indicate that sediments are an overall sink of DOC under oxic condition and a source of DOC under anoxic conditions. Oxic sediments are also a source of DOC at certain times of the year despite being a net sink of DOC when looking at the annual trends. This seasonality in oxic DOC fluxes was found to be related to temperature and will be discussed in detail in the following sections.

As control to the sediment incubation experiments hypolimnion water in bottles was incubated and treated in the same way as sediment cores so as to determine if changes in concentration were due only to the sediments or could also happen in water. *The changes in the controls were below detection limit indicating that changes in solutes concentration in water are very slow therefore controls might not be relevant* *for short term incubations.* The low DOC degradation is both due to the short incubation duration and also the low biodegradability of the DOC. In other studies DOC degradation was observed in long time incubations; 40% after 3.5 years (Kothawala et al. 2012b), 13-20% after 91–131 days (Morling et al. 2016), and 5-24% after 426 days (Bastviken et al. 2003). If controls are to be included in short time incubation then this can be done with less effort.

7.4 Drivers regulating benthic DOC flux

7.4.1 Redox

Exposure of sediment to anoxic overlying water resulted in release of DOC from the sediment into the water. The trend was observed in both Hassel and Rappbode pre-dams at deep sites, which have anoxic hypolimnion following summer stratification. Shallow sites were chosen to be sites that are oxic throughout the year *however in Rappbode in July the shallow site became anoxic and incubation resulted in a similar DOC release trend like the deep site.* Besides following seasonal redox changes additional redox experiments were also carried out. In Rappbode a parallel experiment was done, in which deep site sediments were incubated under different redox conditions and *the result showed that anoxic sediments (in situ conditions) released DOC while the oxic sediment (manipulated redox conditions) actually consumed DOC.* In Rappbode a redox condition manipulation experiment was carried out (Chapter 6). *The sediments for both sites were a sink of DOC under oxic conditions and a source of DOC under anoxic conditions*. DOC release under anoxic condition has been shown in other studies (Skoog and Arias-Esquivel 2009; Yang et al. 2014). There are not so many studies that have quantified DOC fluxes under natural anoxia in freshwater lakes, which makes this result an important contribution to data on anoxic DOC fluxes.

Presence of NO_3^- *in early summer slowed the release of DOC even though the sediments were anoxic* (Chapter 3). Nitrate probably reduced the extent of iron reduction (Andersen 1982; Achtnich et al. 1995; Wauer et al. 2005; Matocha and Coyne 2007) but was a less potent as an oxidant compared to oxygen (Kleeberg and Dudel 1997; Grüneberg et al. 2014). In aquatic systems with higher nitrate levels the nitrate could sustain the redox potential long after oxygen has been depleted thereby delaying release of Fe partners (DOC and phosphorus). This is a research gap that needs to be addressed in future studies.

7.4.2 Temperature

Temperature effects on benthic DOC fluxes can be subdivided into direct temperature effects, and indirect temperature effects. Direct temperature effects occur when DOC is produced as a by-product of mineralization of particulate organic carbon. The *results show a strong temperature dependency of DOC fluxes under oxic conditions. This was also shown by the increasing porewater concentrations with increasing temperatures.* Gudasz et al. (2015) found a strong positive correlation (r^2 = 0.61) between organic carbon (OC) mineralization and temperature in boreal lake sediments. DOC was released in summer under oxic at temperatures above 12°C which should be due to temperature dependent increase in DOC production. Alperin et al. (1994) observed a similar seasonal variation in DOC fluxes, which they attributed to temperature dependant particulate organic matter hydrolysis between spring and autumn. It is unfortunate that in the study areas temperature under anoxic conditions varied only by ±1°C during the year hence it was not possible to investigate temperature effects under *in situ* anoxic conditions. I however speculate that at higher temperature higher DOC fluxes will be observed mainly due to the increasing fraction of DOC from anoxic mineralization. Similar studies in anoxic warmer lakes would close this research gap.

Indirect temperature effects relate to temperature dependency of SO_4^{2-} reduction and Fe reduction. Increasing temperature also increased oxygen consumption. Increased oxygen consumption is known to reduce the oxic sediment layer. This in turn triggers Fe reduction and sulphate reduction. Iron minerals adsorb DOC therefore reduction of Fe will release DOC, which can lead to increased DOC concentration in the water. Furthermore SO_4^{2-} reduction will lead to formation of hydrogen sulphide which can influence DOC by inhibiting bacteria (Canfield 1994) and by immobilization of Fe through formation of iron sulphide (Roden and Edmonds 1997). *A strong negative relationship between temperature and* SO_4^{2-} *flux was observed, indicating the temperature dependency of* SO_4^{2-} *reduction. Furthermore the temperature coefficient (Q10) values of DOC, Fe and* SO_4^{2-} *fluxes were identical which could be an indication of the strong coupling of DOC release to Fe reduction and* SO_4^{2-} *reduction.*

The study also demonstrates that temperature dependency of DOC flux is a localised effect which might not be observed in other systems. This was shown by the weak temperature effects in Rote Mulde. This trend could be a result of the complex temperature and organic substrate interactions which has been suggested in other studies (Sobek et al. 2005).

7.5 Sediment resuspension effect on DOC fluxes

The effect of sediment resuspension on DOC and other solute fluxes in drinking water reservoirs was investigated and it was found out that DOC fluxes following a resuspension event are equivalent to 9-17 days of a diffusive flux under undisturbed *sediment conditions.* This trend has been observed for other solutes (Søndergaard et al. 1992; Reddy et al. 1996). *To the best of my knowledge this study is the first to focus on sediment resuspension effects on DOC and it confirms that resuspension is influencing DOC cycling at the sediment water interface.* The sediment was a source of DOC when resuspension was done under anoxic conditions, a trend which is similar to the observed diffusive flux under anoxia. Interestingly, resuspension under oxic conditions yielded different results for Hassel and Rappbode pre-dams; Hassel was a sink of DOC while Rappbode was a source. The difference in Hassel and Rappbode under oxic condition might be related to the sediment characteristics. Rappbode has coarser sediment particles and a lower organic carbon than Hassel. Rote Mulde was also a sink of DOC like Hassel and the DOC immobilization magnitude was higher than that of Hassel.

Resuspension is regarded as a detrimental process mainly because of mobilization of nutrients into the water column which can cause eutrophication. This is because most of the work on resuspension has been carried in high nutrient systems. *Phosphorus mobilization under oxic conditions was below detection limit in the experiments even in Hassel pre-dam, which is eutrophic.*

Resuspension effects on DOC fluxes were mixed with both mobilization and immobilization occurring. Sediment porewater has a higher DOC concentration than overlying water therefore resuspension is expected to increase the concentration of DOC in the water column. It is known that Fe minerals can adsorb DOC thereby immobilizing it. The sediment is also abundant with heterotrophic bacteria, which can mineralize DOC. *Microbial potential to utilise different substrate groups was investigated and it was found that the potential was higher after resuspension.* The *results however indicate that adsorption of DOC to Fe minerals could be the major mechanism regulating DOC fluxes.*

7.6 DOC quality

Characterization of DOC components is important both for water treatment applications and for understanding carbon cycling processes in the water bodies. Characterization of DOC using the FTICR-MS was employed to gain and insight into DOC quality in drinking water reservoirs in particular the effect of redox conditions on the quality of DOC. *This study, to the best of my knowledge, is among the first to investigate effects of benthic processes on overlying water DOC quality using sediment incubations and FTICR-MS methods. The results show that change in redox conditions affect DOC quality faster than change in DOC degradation. It further underscores the importance of the role of DOC interactions with Fe minerals, which was shown by the concurrent release of DOC and Fe under anoxic conditions mentioned earlier on. This also further supports the observation that Fe rich sediments immobilize DOC from the overlying water after sediment resuspension.*

7.7 Regulatory mechanism of benthic DOC flux

The net DOC flux at the sediment water interface is a sum of the mobilization (production) and immobilization (consumption) processes. Concurrent mobilization of Fe and DOC under anoxic conditions and their immobilization under oxic conditions indicates that the major mechanism regulating benthic DOC flux is adsorption and desorption to mineral surfaces. Chin et al. (1998) observed a strong correlation between Fe and natural organic matter an indication of co-accumulation of Fe and DOC in pore water. This was further demonstrated in the resuspension experiments when DOC was always immobilized under anoxic conditions (Chapter 5). Adsorption and desorption to

Fe minerals has been reported in many other studies (Jonsson 1997; Kaiser and Guggenberger 2000; Kahle et al. 2004; Wagai and Mayer 2007; Lalonde et al. 2012; Chen et al. 2014). Based on this mechanism I give an overview in Fig. 7.1 of how this mechanism works: 1) under different redox conditions, and 2) how temperature can influence these mechanisms. The mechanism shows the interplay between microbial activities and adsorption of DOC to Fe minerals.

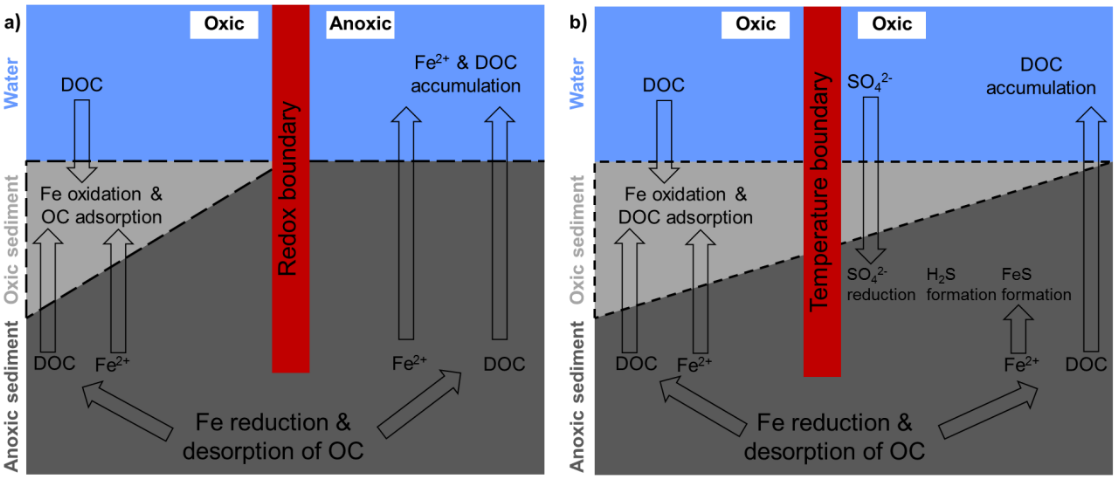

Fig. 7.1. Mechanism regulating benthic DOC fluxes different drivers: (a) under different redox conditions, and (b) under different temperatures

Rote Mulde showed a higher degree of DOC immobilization than the other pre-dams both during incubation and after resuspension. This could be due to the higher concentration of iron in Rote Mulde water compared to the other pre-dams. This is also supported by the lower DOC:Fe molar ratio in Rote Mulde. The higher DOC immobilization in Rote Mulde could also be due to the quality of DOC. Rote Mulde had a weak DOC flux and temperature correlation, which might indicate that larger portion of DOC is allochthonous rather than autochthonous. Allochthonous DOC is characterized by high molecular weight, aromatic moieties and carboxyl groups which favour its preferential adsorption to Fe minerals (Kaiser et al. 1997; Maurice et al. 2002; Guo and Chorover 2003). The more allochthonous nature of Rote Mulde DOC was also indicated by a higher $SUVA_{254nm}$ (5 L mg^{-1} C m^{-1}). The $SUVA_{254nm}$ values above > 4 L mg^{-1} C m^{-1} have been shown to indicate removal of >50% of DOC by coagulation in water treatment processes (Edzwald and Tobiason 1999).

7.8 Future research

In this section I focus on research gaps identified from the findings. This work was carried out in reservoirs with an anoxic hypolimnion and temperatures ranging between 4-6^{o}C. Therefore temperature effects under anoxic conditions at *in situ* temperatures could not be investigated. Similar investigations in warmer reservoirs with an anoxic hypolimnion would close this research gap. Another aspect in relation to anoxia is the role of nitrate in keeping the sediment redox potential high after oxygen depletion. Release of DOC under anoxia and presence of nitrate was lower than release under anoxia and no nitrate conditions. Anoxia and presence of nitrate only occurred once hence it would be interesting to investigate this effect under *in situ* conditions or through nitrate manipulation in laboratory experiments.

Sediment resuspension effects varied in the three investigated pre-dams, with high DOC immobilization in the oligotrophic Rote Mulde, low DOC immobilization in the eutrophic Hassel, and the DOC mobilization in the Rappbode sediment. The findings identify adsorption to Fe as the main regulating mechanism. To elucidate further on this mechanism a closer look using sediment mineralogy methods would be helpful to gain insight into; speciation of Fe minerals, their sorption capacities, and potential interactions with clay minerals and how they affect sorption.

The results of this study are based on manual sediment resuspension in the cores and offer an insight more into the effects of resuspension. It does not quantify the actual resuspension in the pre-dams. Therefore it is important that future studies could make use of *in situ* sediment traps placed near the sediment surface to quantify *in situ* sediment resuspension.

Microbial potential to degrade organic substrates increased after sediment resuspension and this is attributed to potential introduction of benthic heterotrophic microorganisms into the overlying water after resuspension. More in depth microbiology studies can be employed to isolate the species of heterotrophic bacteria involved, quantify extracellular enzymes already in the sediment that are introduced into the overlying water during resuspension. Also interesting would be to quantify potential bacteria stripping from the water that can occur when the bacteria attaches to particles and eventually get deposited in the sediment.

7.9 Implications and outlook

In this section I look at the processes investigated in this study in the light of the benthic carbon cycling processes. I also focus on the role of this study in the context of global water issues both current and envisaged.

The study was undertaken to gain a better understanding of the benthic carbon cycling and I investigated the major processes and drivers involved in benthic carbon cycling. It is clear from the results that benthic mobilization/immobilization is a negligible process compared to DOC imports from the catchment. The reservoirs also have low fluxes of benthic nitrogen and phosphorus. Therefore interventions in the reservoirs are not necessary at the moment. However if DOC concentrations reach levels that threaten aquatic ecosystems, a possible intervention would be application of metal coagulants to immobilize DOC from the water into the sediment.

Climate change will result in warmer temperatures. This will trigger stronger/longer summer stratification, and an increase in productivity of water bodies, both which leads to anoxia. As a result an increase in benthic DOC release is expected. Warmer temperatures will consequently lead to water level fluctuations. Water level drawdown will diminish area of anoxic sediments and probably counteract DOC increase. However, effects of water level fluctuations are complicated since lower water levels might increase the annual sediment resuspension as more and more sediment become exposed to wind induced resuspension. This will lead to potential DOC immobilization/mobilization depending on the reservoir system. It is clear that there are a lot of uncertainties to climate change effects. The results of this study will be helpful to those who want to simulate future scenarios of climate change effects on the lake biogeochemical cycles, and also provide a basis for further research.

Erosion and siltation of lakes and reservoirs occurs in most parts of the world, with mean annual capacity loss rates of up to 2% (Wisser et al. 2013). However, the majority of reservoirs do not have pre-dams. There is likelihood that more pre-dams will be constructed to avert the negative impacts of siltation and eutrophication. The finding of this thesis on mobilisation of DOC and other solutes under anoxia will be useful in shaping construction designs that prevent anoxia in line with measures to reduce internal P loading.

Increasing energy demand and water shortages in some parts of the world will likely lead to construction of more dams and reservoirs. At least 3700 major dams (capacity >1MW) are under construction or planned in emerging economies (Zarfl et al. 2015). Most areas with an expected increase in dams are not among those experiencing increasing DOC concentration. However the findings on the role of redox and temperature still remain important overall when considering mobilization/ immobilization of nutrients and toxic metals, and potential emission of greenhouse gases.

References

Achtnich, C., F. Bak, and R. Conrad. 1995. Competition for electron donors among nitrate reducers, ferric iron reducers, sulfate reducers, and methanogens in anoxic paddy soil. Biol Fertil Soils **19:** 65-72. doi:10.1007/BF00336349

Aller, R. C. 1994. Bioturbation and remineralization of sedimentary organic-matter - effects of redox oscillation. Chemical Geology **114:** 331-345. doi:10.1016/0009-2541(94)90062-0

Alperin, M. J., D. B. Albert, and C. S. Martens. 1994. Seasonal variations in production and consumption rates of dissolved organic carbon in an organic-rich coastal sediment. Geochimica et Cosmochimica Acta **58:** 4909-4930. doi:10.1016/0016-7037(94)90221-6

Alperin, M. J. and others 1999. Benthic fluxes and porewater concentration profiles of dissolved organic carbon in sediments from the North Carolina continental slope. Geochimica et Cosmochimica Acta **63:** 427-448. doi:10.1016/S0016-7037(99)00032-0

Andersen, J. M. 1982. Effect of nitrate concentration in lake water on phosphate release from the sediment. Water Research **16:** 1119-1126. doi:10.1016/0043-1354(82)90128-2

Anderson, N. J., H. Bennion, and A. F. Lotter. 2014. Lake eutrophication and its implications for organic carbon sequestration in Europe. Global Change Biology **20:** 2741-2751. doi:10.1111/gcb.12584

Andersson, S., I. Valeur, and I. Nilsson. 1994. Influence of lime on soil respiration, leaching of DOC, and C/S relationships in the mor humus of a haplic podsol. Environment International **20:** 81-88. doi:10.1016/0160-4120(94)90070-1

Baborowski, M., V. Simeonov, and J. W. Einax. 2012. Assessment of water quality in the Elbe river at flood water conditions based on cluster analysis, principle components analysis, and source apportionment. CLEAN – Soil, Air, Water **40:** 373-380. doi:10.1002/clen.201100085

Baham, J., and G. Sposito. 1994. Adsorption of dissolved organic-carbon extracted from sewage-sludge on montmorillonite and kaolinite in the presence of metal-ions. Journal of Environmental Quality **23:** 147-153. doi:10.2134/jeq1994.00472425002300010023x

Bastviken, D., M. Olsson, and L. Tranvik. 2003. Simultaneous Measurements of Organic Carbon Mineralization and Bacterial Production in Oxic and Anoxic Lake Sediments. Microbial Ecology **46:** 73-82. doi:10.1007/s00248-002-1061-9

Bastviken, D., L. Persson, G. Odham, and L. Tranvik. 2004. Degradation of dissolved organic matter in oxic and anoxic lake water. Limnology and Oceanography **49:** 109-116. doi:10.4319/lo.2004.49.1.0109

Bauer, M., and C. Blodau. 2006. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. Science of The Total Environment **354:** 179-190. doi:10.1016/j.scitotenv.2005.01.027

Benndorf, J., and K. Pütz. 1987a. Control of eutrophication of lakes and reservoirs by means of pre-dams—I. Mode of operation and calculation of the nutrient elimination capacity. Water Research **21:** 829-838. doi:10.1016/0043-1354(87)90159-X

---. 1987b. Control of eutrophication of lakes and reservoirs by means of Pre-Dams—II. Validation of the phosphate removal model and size optimization. Water Research **21:** 839-842. doi:10.1016/0043-1354(87)90160-6

Berg, P., N. Risgaard-Petersen, and S. Rysgaard. 1998. Interpretation of measured concentration profiles in sediment pore water. Limnology and Oceanography **43:** 1500-1510. doi:10.4319/lo.1998.43.7.1500

Bertilsson, S., and J. B. Jones Jr. 2003. 1 - Supply of Dissolved Organic Matter to Aquatic Ecosystems: Autochthonous Sources A2 - Findlay, Stuart E.G, p. 3-24. *In* R. L. Sinsabaugh [ed.], Aquatic Ecosystems. Academic Press.

Blodau, C., and S. Peiffer. 2003. Thermodynamics and organic matter: constraints on neutralization processes in sediments of highly acidic waters. Applied Geochemistry **18:** 25-36. doi:10.1016/S0883-2927(02)00052-5

Bloesch, J. 1995. Mechanisms, measurement and importance of sediment resuspension in lakes. Marine and Freshwater Research **46:** 295-304. doi:10.1071/MF9950295

Bondarenko, A., D. Sani, and M. L. Ruello. 2011. Design and calibration of an organic diffusive probe to extend the diffusion gradient technique to organic pollutants. International Journal of Environmental Research and Public Health **8:** 3318-3332. doi:10.3390/ijerph8083318

Boto, K. G., D. M. Alongi, and A. L. J. Nott. 1989. Dissolved organic carbon-bacteria interactions at sediment-water interface in a tropical mangrove system. Marine Ecology Progress Series **51:** 243-251. doi:10.3354/meps051243

Burdige, D. J., M. J. Alperin, J. Homstead, and C. S. Martens. 1992. The role of benthic fluxes of dissolved organic carbon in oceanic and sedimentary carbon cycling. Geophysical Research Letters **19:** 1851-1854. doi:10.1029/92GL02159

Burdige, D. J., and J. Homstead. 1994. Fluxes of dissolved organic carbon from Chesapeake Bay sediments. Geochimica Et Cosmochimica Acta **58:** 3407-3424. doi:10.1016/0016-7037(94)90095-7

Canfield, D. E. 1994. Factors influencing organic-carbon preservation in marine-sediments. Chemical Geology **114:** 315-329. doi:10.1016/0009-2541(94)90061-2

Carter, H. T., E. Tipping, J.-F. Koprivnjak, M. P. Miller, B. Cookson, and J. Hamilton-Taylor. 2012. Freshwater DOM quantity and quality from a two-component model of UV absorbance. Water Research **46:** 4532-4542. doi:10.1016/j.watres.2012.05.021

Catalan, N., R. Marce, D. N. Kothawala, and L. J. Tranvik. 2016. Organic carbon decomposition rates controlled by water retention time across inland waters. Nature Geosci (in press). doi:10.1038/ngeo2720

Chen, C., J. J. Dynes, J. Wang, and D. L. Sparks. 2014. Properties of Fe-organic matter associations via coprecipitation versus adsorption. Environmental Science & Technology **48:** 13751-13759. doi:10.1021/es503669u

Chin, Y.-P., G. Aiken, and E. O'loughlin. 1994. Molecular Weight, Polydispersity, and Spectroscopic Properties of Aquatic Humic Substances. Environmental Science & Technology **28:** 1853-1858. doi:10.1021/es00060a015

Chin, Y. P., S. J. Traina, C. R. Swank, and D. Backhus. 1998. Abundance and properties of dissolved organic matter in pore waters of a freshwater wetland. Limnology and Oceanography **43:** 1287-1296. doi:10.4319/lo.1998.43.6.1287

Clow, D. W. and others 2015. Organic carbon burial in lakes and reservoirs of the Conterminous United States. Environmental Science & Technology **49:** 7614-7622. doi:10.1021/acs.est.5b00373

Cole, J. J., M. L. Pace, S. R. Carpenter, and J. F. Kitchell. 2000. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. Limnology and Oceanography **45:** 1718-1730. doi:10.4319/lo.2000.45.8.1718

Cortés-Francisco, N. and others 2014. High-field FT-ICR mass spectrometry and NMR spectroscopy to characterize DOM removal through a nanofiltration pilot plant. Water Research **67:** 154-165. doi:10.1016/j.watres.2014.08.046

Couture, S., D. Houle, and C. Gagnon. 2011. Increases of dissolved organic carbon in temperate and boreal lakes in Quebec, Canada. Environmental Science and Pollution Research **19:** 361-371. doi:10.1007/s11356-011-0565-6

Dadi, T., K. Friese, K. Wendt-Potthoff, and M. Koschorreck. 2016. Benthic dissolved organic carbon fluxes in a drinking water reservoir. Limnol. Oceanogr.**:** 445-459. doi:10.1002/lno.10224

Davis, C. C., W. R. Knocke, and M. Edwards. 2001. Implications of aqueous silica sorption to iron hydroxide: mobilization of iron colloids and interference with sorption of arsenate and humic substances. Environmental Science & Technology **35:** 3158-3162. doi:10.1021/es0018421

Davis, J. A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. Geochimica Et Cosmochimica Acta **46:** 2381-2393. doi:10.1016/0016-7037(82)90209-5

De Vicente, I., L. Cruz-Pizarro, and F. J. Rueda. 2010. Sediment resuspension in two adjacent shallow coastal lakes: controlling factors and consequences on phosphate dynamics. Aquatic Science **72:** 21-31. doi:10.1007/s00027-009-0107-1

Del Giorgio, P. A., J. J. Cole, N. F. Caraco, and R. H. Peters. 1999. Linking planktonic biomass and metabolism to net gas fluxes in northern temperate lakes. Ecology **80:** 1422-1431. doi:10.1890/0012-9658(1999)080[1422:lpbamt]2.0.co;2

Demarty, M., and Y. T. Prairie. 2009. In situ dissolved organic carbon (DOC) release by submerged macrophyte-epiphyte communities in southern Quebec lakes. Canadian Journal of Fisheries and Aquatic Sciences **66:** 1522-1531. doi:10.1139/f09-099

Den Heyer, C., and J. Kalff. 1998. Organic matter mineralization rates in sediments: A within- and among-lake study. Limnology and Oceanography **43:** 695-705. doi:10.4319/lo.1998.43.4.0695

DIN_38404-3:2005-07. 2005. German standard methods for the examination of water, waste water and sludge - Physical and physical-chemical parameters (group C) - Part 3: Determination of absorption in the range of the ultraviolet radiation, Spectral absorptions coefficient (C 3). Beuth Verlag.

DIN_EN_1484:1997-08. 1997. Water analysis - Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC); German version EN 1484-1997. Beuth Verlag.

DIN_EN_ISO_10304-1. 2009. Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate (ISO 10304-1:2007); German version EN ISO 10304-1:2009. Beuth Verlag.

DIN_EN_ISO_11885:2009-09. 2009. Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885:2007); German version EN ISO 11885:2009. Beuth Verlag.

Edzwald, J. K., and J. E. Tobiason. 1999. Enhanced coagulation: US requirements and a broader view. Water Science and Technology **40:** 63-70. doi:10.1016/s0273-1223(99)00641-1

Eikebrokk, B., R. D. Vogt, and H. Liltved. 2004. NOM increase in Northern European source waters: discussion of possible causes and impacts on coagulation/contact filtration processes. Water Science and Technology: Water Supply **4:** 47-54. doi

Einsele, W. 1936. Ueber die Beziehungen des Eisenkreislaufs zum Phosphatekreislauf im eutrophen See. Archiv für Hydrobiologie **29:** 664–686. doi

Escobar, I. C., A. A. Randall, and J. S. Taylor. 2001. Bacterial growth in distribution systems: effect of assimilable organic carbon and biodegradable dissolved organic carbon. Environmental Science & Technology **35:** 3442-3447. doi:10.1021/es0106669

Evans, C. D., P. J. Chapman, J. M. Clark, D. T. Monteith, and M. S. Cresser. 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. Global Change Biology **12:** 2044-2053. doi:10.1111/j.1365-2486.2006.01241.x

Evans, C. D. and others 2012. Acidity controls on dissolved organic carbon mobility in organic soils. Global Change Biology **18:** 3317-3331. doi:10.1111/j.1365-2486.2012.02794.x

Evans, C. D., D. T. Monteith, and D. M. Cooper. 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. Environmental Pollution **137:** 55-71. doi:10.1016/j.envpol.2004.12.031

Fellman, J. B., E. Hood, and R. G. M. Spencer. 2010. Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. Limnology and Oceanography **55:** 2452-2462. doi:10.4319/lo.2010.55.6.2452

Fenner, N., and C. Freeman. 2013. Carbon preservation in humic lakes; a hierarchical regulatory pathway. Global Change Biology **19:** 775-784. doi:10.1111/gcb.12066

Findlay, S. E. G. 2005. Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition? Frontiers in Ecology and the Environment **3:** 133-137. doi:10.1890/1540-9295(2005)003[0133:ictith]2.0.co;2

Fischer, J., R. Krogman, and M. Quist. 2013. Influences of native and non-native benthivorous fishes on aquatic ecosystem degradation. Hydrobiologia **711:** 187-199. doi:10.1007/s10750-013-1483-z

Freeman, C., C. D. Evans, D. T. Monteith, B. Reynolds, and N. Fenner. 2001. Export of organic carbon from peat soils. Nature **412:** 785-785. doi:10.1038/35090628

Freeman, C. and others 2004. Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. Nature **430:** 195-198. doi:10.1038/nature02707

Friese, K. and others 2014. Ecological response of two hydro-morphological similar pre-dams to contrasting land-use in the Rappbode reservoir system (Germany). International Review of Hydrobiology **99:** 335-349. doi:10.1002/iroh.201301672

Galapate, R. P., A. U. Baes, and M. Okada. 2001. Transformation of dissolved organic matter during ozonation: effects on trihalomethane formation potential. Water Research **35:** 2201-2206. doi:10.1016/S0043-1354(00)00489-9

Gale, P. M., and K. R. Reddy. 1994. Carbon flux between sediment and water column of a shallow, subtropical, hypereutrophic lake. Journal of Environmental Quality **23:** 965-972. doi:10.2134/jeq1994.00472425002300050017x

Gough, R., P. J. Holliman, N. Willis, and C. Freeman. 2014. Dissolved organic carbon and trihalomethane precursor removal at a UK upland water treatment works. Science of the Total Environment **468:** 228-239. doi:10.1016/j.scitotenv.2013.08.048

Grafe, M., M. J. Eick, and P. R. Grossl. 2001. Adsorption of arsenate (V) and arsenite (III) on goethite in the presence and absence of dissolved organic carbon. Soil Science Society of America Journal **65:** 1680-1687. doi:10.2134/jeq2002.1115

Grüneberg, B., T. Dadi, C. Lindim, and H. Fischer. 2014. Effects of nitrogen and phosphorus load reduction on benthic phosphorus release in a riverine lake. Biogeochemistry**:** 1-18. doi:10.1007/s10533-014-0062-3

Gu, B., J. Schmitt, Z. Chen, L. Liang, and J. F. Mccarthy. 1994. Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. Environmental Science & Technology **28:** 38-46. doi:10.1021/es00050a007

Gudasz, C., S. Sobek, D. Bastviken, B. Koehler, and L. J. Tranvik. 2015. Temperature sensitivity of organic carbon mineralization in contrasting lake sediments. Journal of Geophysical Research-Biogeosciences **120:** 1215-1225. doi:10.1002/2015jg002928

Guggenberger, G., K. Kaiser, and W. Zech. 1998. Mobilization and immobilization of dissolved organic matter in forest soils. Zeitschrift Fur Pflanzenernahrung Und Bodenkunde **161:** 401-408. doi:10.1002/jpln.1998.3581610408

Guillemette, F., and P. A. Del Giorgio. 2012. Simultaneous consumption and production of fluorescent dissolved organic matter by lake bacterioplankton. Environmental Microbiology **14:** 1432-1443. doi:10.1111/j.1462-2920.2012.02728.x

Guo, M. X., and J. Chorover. 2003. Transport and fractionation of dissolved organic matter in soil columns. Soil Science **168:** 108-118. doi:10.1097/00010694-200302000-00005

Halbedel, S., and M. Koschorreck. 2013. Regulation of CO2 emissions from temperate streams and reservoirs. Biogeosciences **10:** 7539-7551. doi:10.5194/bg-10-7539-2013

Hammond, D. E., K. M. Cummins, J. Mcmanus, W. M. Berelson, G. Smith, and F. Spagnoli. 2004. Methods for measuring benthic nutrient flux on the California Margin: Comparing shipboard core incubations to in situ lander results. Limnology and Oceanography-Methods **2:** 146-159. doi:10.4319/lom.2004.2.146

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

Heathcote, A. J., and J. A. Downing. 2012. Impacts of eutrophication on carbon burial in freshwater lakes in an intensively agricultural landscape. Ecosystems **15:** 60-70. doi:10.1007/s10021-011-9488-9

Herzsprung, P., K. Friese, G. Packroff, M. Schimmele, K. Wendt-Potthoff, and M. Winkler. 1998. Vertical and annual distribution of ferric and ferrous iron in acidic mining lakes. Acta Hydrochimica Et Hydrobiologica **26:** 253-262. doi

Herzsprung, P., N. Hertkorn, K. Friese, and P. Schmitt-Kopplin. 2010. Photochemical degradation of natural organic sulfur compounds (CHOS) from iron-rich mine pit lake pore waters - an initial understanding from evaluation of single-elemental formulae using ultra-high-resolution mass spectrometry. Rapid Communications in Mass Spectrometry **24:** 2909-2924. doi:10.1002/rcm.4719

Herzsprung, P., N. Hertkorn, W. Von Tuempling, M. Harir, K. Friese, and P. Schmitt-Kopplin. 2014. Understanding molecular formula assignment of Fourier transform ion cyclotron resonance mass spectrometry data of natural organic matter from a chemical point of view. Analytical and Bioanalytical Chemistry **406:** 7977-7987. doi:10.1007/s00216-014-8249-y

Herzsprung, P. and others 2012a. Variations of DOM quality in inflows of a drinking water reservoir: Linking of van Krevelen diagrams with EEMF spectra by rank correlation. Environmental Science & Technology **46:** 5511-5518. doi:10.1021/es300345c

Herzsprung, P. and others 2012b. Variations of DOM Quality in inflows of a drinking water reservoir: linking of van Krevelen diagrams with EEMF spectra by rank correlation. Environmental Science & Technology **46:** 5511-5518. doi:10.1021/es300345c

Holmer, M., and P. Storkholm. 2001. Sulphate reduction and sulphur cycling in lake sediments: a review. Freshwater Biology **46:** 431-451. doi:10.1046/j.1365-2427.2001.00687.x

Hruška, J., S. Köhler, H. Laudon, and K. Bishop. 2003. Is a aniversal model of organic acidity possible: comparison of the acid/base properties of dissolved organic carbon in the boreal and temperate zones. Environmental Science & Technology **37:** 1726-1730. doi:10.1021/es0201552

Hunt, J. F., T. Ohno, Z. He, C. W. Honeycutt, and D. B. Dail. 2007. Inhibition of phosphorus sorption to goethite, gibbsite, and kaolin by fresh and decomposed organic matter. Biol Fertil Soils **44:** 277-288. doi:10.1007/s00374-007-0202-1

Jiang, D., Q. Huang, P. Cai, X. Rong, and W. Chen. 2007. Adsorption of Pseudomonas putida on clay minerals and iron oxide. Colloids and Surfaces B: Biointerfaces **54:** 217-221. doi:10.1016/j.colsurfb.2006.10.030

Jonsson, A. 1997. Fe and Al sedimentation and their importance as carriers for P, N and C in a large humic lake in northern Sweden, p. 283-295. *In* R. D. Evans, J. Wisniewski and J. Wisniewski [eds.], The Interactions Between Sediments and Water. Springer Netherlands.

Jonsson, A., M. Meili, A.-K. Bergström, and M. Jansson. 2001. Whole-lake mineralization of allochthonous and autochthonous organic carbon in a large humic lake (örträsket, N. Sweden). Limnology and Oceanography **46:** 1691-1700. doi:10.4319/lo.2001.46.7.1691

Kahle, M., M. Kleber, and R. Jahn. 2004. Retention of dissolved organic matter by phyllosilicate and soil clay fractions in relation to mineral properties. Organic Geochemistry **35:** 269-276. doi:10.1016/j.orggeochem.2003.11.008

Kaiser, K., and G. Guggenberger. 2000. The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. Organic Geochemistry **31:** 711-725. doi:10.1016/s0146-6380(00)00046-2

Kaiser, K., G. Guggenberger, L. Haumaier, and W. Zech. 1997. Dissolved organic matter sorption on subsoils and minerals studied by C-13-NMR and DRIFT spectroscopy.

European Journal of Soil Science **48:** 301-310. doi:10.1111/j.1365-2389.1997.tb00550.x

Kaiser, K., M. Kaupenjohann, and W. Zech. 2001. Sorption of dissolved organic carbon in soils: effects of soil sample storage, soil-to-solution ratio, and temperature. Geoderma **99:** 317-328. doi:10.1016/S0016-7061(00)00077-X

Kaiser, K., and W. Zech. 2000. Dissolved organic matter sorption by mineral constituents of subsoil clay fractions. Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde **163:** 531-535. doi:10.1002/1522-2624(200010)163:5<531::aid-jpln531>3.0.co;2-n

Kalbitz, K., J. Schmerwitz, D. Schwesig, and E. Matzner. 2003. Biodegradation of soil-derived dissolved organic matter as related to its properties. Geoderma **113:** 273-291. doi:10.1016/S0016-7061(02)00365-8

Kalbitz, K., S. Solinger, J. H. Park, B. Michalzik, and E. Matzner. 2000. Controls on the dynamics of dissolved organic matter in soils: A review. Soil Science **165:** 277-304. doi:10.1097/00010694-200004000-00001

Kellerman, A. M., D. N. Kothawala, T. Dittmar, and L. J. Tranvik. 2015. Persistence of dissolved organic matter in lakes related to its molecular characteristics. Nature Geosci **8:** 454-457. doi:10.1038/ngeo2440

Kleeberg, A., and G. E. Dudel. 1997. Changes in extent of phosphorus release in a shallow lake (Lake Grosser Muggelsee; Germany, Berlin) due to climatic factors and load. Marine Geology **139:** 61-75. doi:10.1016/s0025-3227(96)00099-0

Knorr, K. H. 2013. DOC-dynamics in a small headwater catchment as driven by redox fluctuations and hydrological flow paths – are DOC exports mediated by iron reduction/oxidation cycles? Biogeosciences **10:** 891-904. doi:10.5194/bg-10-891-2013

Koelmans, A. A., and L. Prevo. 2003. Production of dissolved organic carbon in aquatic sediment suspensions. Water Research **37:** 2217-2222. doi:10.1016/S0043-1354(02)00581-X

Kõiv, T., T. Nõges, and A. Laas. 2011. Phosphorus retention as a function of external loading, hydraulic turnover time, area and relative depth in 54 lakes and reservoirs. Hydrobiologia **660:** 105-115. doi:10.1007/s10750-010-0411-8

Komada, T., and C. E. Reimers. 2001. Resuspension-induced partitioning of organic carbon between solid and solution phases from a river–ocean transition. Marine Chemistry **76:** 155-174. doi:10.1016/S0304-4203(01)00055-X

Koschinsky, A. and others 2001. Experiments on the influence of sediment disturbances on the biogeochemistry of the deep-sea environment. Deep Sea Research Part II: Topical Studies in Oceanography **48:** 3629-3651. doi:10.1016/S0967-0645(01)00060-1

Koschorreck, M., E. Bozau, R. Froemmichen, W. Geller, P. Herzsprung, and K. Wendt-Potthoff. 2007. Processes at the sediment water interface after addition of organic matter and lime to an acid mine pit lake mesocosm. Environmental Science & Technology **41:** 1608-1614. doi:10.1021/es0614823

Kothawala, D. N., C. Roehm, C. Blodau, and T. R. Moore. 2012a. Selective adsorption of dissolved organic matter to mineral soils. Geoderma **189:** 334-342. doi:10.1016/j.geoderma.2012.07.001

Kothawala, D. N., E. Von Wachenfeldt, B. Koehler, and L. J. Tranvik. 2012b. Selective loss and preservation of lake water dissolved organic matter fluorescence during long-term dark incubations. Science of The Total Environment **433:** 238-246. doi:10.1016/j.scitotenv.2012.06.029

Lalonde, K., A. Mucci, A. Ouellet, and Y. Gelinas. 2012. Preservation of organic matter in sediments promoted by iron. Nature **483:** 198-200. doi:10.1038/nature10855

Larsen, S., T. Andersen, and D. O. Hessen. 2011. Climate change predicted to cause severe increase of organic carbon in lakes. Global Change Biology **17:** 1186-1192. doi:10.1111/j.1365-2486.2010.02257.x

Laskov, C., C. Herzog, J. Lewandowski, and M. Hupfer. 2007. Miniaturized photometrical methods for the rapid analysis of phosphate, ammonium, ferrous iron, and sulfate in pore water of freshwater sediments. Limnology and Oceanography-Methods **5:** 63-71. doi:10.4319/lom.2007.5.63

Laudon, H. and others 2011. Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: The Role of Processes, Connectivity, and Scaling. Ecosystems **14:** 880-893. doi:10.1007/s10021-011-9452-8

Le Moigne, F. a. C., M. Gallinari, E. Laurenceau, and C. L. De La Rocha. 2013. Enhanced rates of particulate organic matter remineralization by microzooplankton are diminished by added ballast minerals. Biogeosciences **10:** 5755-5765. doi:10.5194/bg-10-5755-2013

Liang, Y., X. Liu, H. Xiao, X. Gao, W. Li, and J. Xiong. 2016. Impact of high water level fluctuations on stable isotopic signature of POM and source identification in a floodplain lake—Bang Lake (Poyang Lake). Environmental Earth Sciences **75:** 1-12. doi:10.1007/s12665-015-4847-z

Lind, O. T. 2002. Reservoir Zones: Microbial Production and Trophic State. Lake and Reservoir Management **18:** 129-137. doi:10.1080/07438140209354143

Lindstrom, E. S., M. P. Kamst-Van Agterveld, and G. Zwart. 2005. Distribution of typical freshwater bacterial groups is associated with pH, temperature, and lake water retention time. Applied and Environmental Microbiology **71:** 8201-8206. doi:10.1128/aem.71.12.8201-8206.2005

Litchman, E. 2003. Competition and coexistence of phytoplankton under fluctuating light: experiments with two cyanobacteria. Aquatic Microbial Ecology **31:** 241-248. doi:10.3354/ame031241

Maloney, K. O., D. P. Morris, C. O. Moses, and C. L. Osburn. 2005. The role of iron and dissolved organic carbon in the absorption of ultraviolet radiation in humic lake water. Biogeochemistry **75:** 393-407. doi:10.1007/s10533-005-1675-3

Matilainen, A., E. T. Gjessing, T. Lahtinen, L. Hed, A. Bhatnagar, and M. Sillanpää. 2011. An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. Chemosphere **83:** 1431-1442. doi:10.1016/j.chemosphere.2011.01.018

Matocha, C. J., and M. S. Coyne. 2007. Short-term response of soil iron to nitrate addition. Soil Science Society of America Journal **71:** 108-117. doi:10.2136/sssaj2005.0170

Maurice, P. A., S. E. Cabaniss, J. Drummond, and E. Ito. 2002. Hydrogeochemical controls on the variations in chemical characteristics of natural organic matter at a small freshwater wetland. Chemical Geology **187:** 59-77. doi:10.1016/s0009-2541(02)00016-5

Mc Dowell, W. M. 1985. Kinetics and mechanisms of dissolved organic carbon retention in a headwater stream. Biogeochemistry **1:** 329-352. doi:10.1007/BF02187376

Mcknight, D. M., E. Hood, and L. Klapper. 2003. 3 - Trace Organic Moieties of Dissolved Organic Material in Natural Waters A2 - Findlay, Stuart E.G, p. 71-96. *In* R. L. Sinsabaugh [ed.], Aquatic Ecosystems. Academic Press.

Mclatchey, G. P., and K. R. Reddy. 1998. Regulation of organic matter decomposition and nutrient release in a wetland soil. Journal of Environmental Quality **27:** 1268-1274. doi:10.2134/jeq1998.00472425002700050036x

Middelburg, J. J. 1989. A simple rate model for organic matter decomposition in marine sediments. Geochimica et Cosmochimica Acta **53:** 1577-1581. doi:10.1016/0016-7037(89)90239-1

Monteith, D. T. and others 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature **450:** 537-U539. doi:10.1038/nature06316

Morling, K., N. Kamjunke, and J. Tittel. 2016. A simplified method of recovering CO2 from bacterioplankton respiration for isotopic analysis. Journal of Microbiological Methods **121:** 8-10. doi:10.1016/j.mimet.2015.12.008

Mortimer, C. H. 1942. The exchange of dissolved substances between mud and water in lakes. Journal of Ecology **30:** 147-201. doi:10.2307/2256691

Mulholland, P. J., and J. W. Elwood. 1982. The role of lake and reservoir sediments as sinks in the perturbed global carbon cycle. Tellus **34:** 490-499. doi:10.1111/j.2153-3490.1982.tb01837.x

Murtagh, F., and P. Legendre. 2014. Ward’s hierarchical agglomerative clustering method: which algorithms implement Ward’s criterion? Journal of Classification **31:** 274-295. doi:10.1007/s00357-014-9161-z

Musolff, A., C. Schmidt, B. Selle, and J. H. Fleckenstein. 2015. Catchment controls on solute export. Advances in Water Resources **86, Part A:** 133-146. doi:10.1016/j.advwatres.2015.09.026

Ogilvie, B. G., and S. F. Mitchell. 1998. Does sediment resuspension have persistent effects on phytoplankton? Experimental studies in three shallow lakes. Freshwater Biology **40:** 51-63. doi:10.1046/j.1365-2427.1998.00331.x

Paul, L. 2003. Nutrient elimination in pre-dams: results of long term studies. Hydrobiologia **504:** 289-295. doi:10.1023/B:HYDR.0000008528.34920.b2

Persson, A., and J. M. Svensson. 2006. Effects of benthivorous fish on biogeochemical processes in lake sediments. Freshwater Biology **51:** 1298-1309. doi:10.1111/j.1365-2427.2006.01569.x

Peura, S., H. Nykanen, P. Kankaala, A. Eiler, M. Tiirola, and R. I. Jones. 2014. Enhanced greenhouse gas emissions and changes in plankton communities following an experimental increase in organic carbon loading to a humic lake. Biogeochemistry **118:** 177-194. doi:DOI 10.1007/s10533-013-9917-2

Poulin, B. A., J. N. Ryan, and G. R. Aiken. 2014. Effects of Iron on Optical Properties of Dissolved Organic Matter. Environmental Science & Technology **48:** 10098-10106. doi:10.1021/es502670r

Pütz, K., and J. Benndorf. 1998. The importance of pre-reservoirs for the control of eutrophication of reservoirs. Water Science and Technology **37:** 317-324. doi:10.1016/S0273-1223(98)00039-0

Rahman, I., S. Ndiongue, X. Jin, M. I. Van Dyke, W. B. Anderson, and P. M. Huck. 2014. Fouling of low-pressure membranes during drinking water treatment: effect of NOM components and biofiltration pretreatment. Water Science and Technology: Water Supply **14:** 453-460. doi:10.2166/ws.2013.221

Ramseier, M. K., A. Peter, J. Traber, and U. Von Gunten. 2011. Formation of assimilable organic carbon during oxidation of natural waters with ozone, chlorine dioxide, chlorine, permanganate, and ferrate. Water Research **45:** 2002-2010. doi:10.1016/j.watres.2010.12.002

Rasmussen, H., and B. B. Jorgensen. 1992. Microelectrode studies of seasonal oxygen-uptake in a coastal sediment - role of molecular-diffusion. Marine Ecology Progress Series **81:** 289-303. doi:10.3354/meps081289

Read, J. S. and others 2011. Derivation of lake mixing and stratification indices from high-resolution lake buoy data. Environmental Modelling & Software **26:** 1325-1336. doi:10.1016/j.envsoft.2011.05.006

Reddy, K. R., M. M. Fisher, and D. Ivanoff. 1996. Resuspension and diffusive flux of nitrogen and phosphorus in a hypereutrophic lake. Journal of Environmental Quality **25:** 363-371. doi:10.2134/jeq1996.00472425002500020022x

Richardson, S. D., M. J. Plewa, E. D. Wagner, R. Schoeny, and D. M. Demarini. 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. Mutation Research/Reviews in Mutation Research **636:** 178-242. doi:10.1016/j.mrrev.2007.09.001

Riedel, T., D. Zak, H. Biester, and T. Dittmar. 2013. Iron traps terrestrially derived dissolved organic matter at redox interfaces. Proceedings of the National Academy of Sciences of the United States of America **110:** 10101-10105. doi:10.1073/pnas.1221487110

Rinke, K. and others 2013. Reservoirs as sentinels of catchments: the Rappbode Reservoir Observatory (Harz Mountains, Germany). Environmental Earth Sciences **69:** 523-536. doi:10.1007/s12665-013-2464-2

Roden, E. E., and J. W. Edmonds. 1997. Phosphate mobilization in iron-rich anaerobic sediments: Microbial Fe(III) oxide reduction versus iron-sulfide formation. Archiv Fur Hydrobiologie **139:** 347-378. doi

Saadi, I., M. Borisover, R. Armon, and Y. Laor. 2006. Monitoring of effluent DOM biodegradation using fluorescence, UV and DOC measurements. Chemosphere **63:** 530-539. doi:10.1016/j.chemosphere.2005.07.075

Sachse, A., D. Babenzien, G. Ginzel, J. Gelbrecht, and C. E. W. Steinberg. 2001. Characterization of dissolved organic carbon (DOC) in a dystrophic lake and an adjacent fen. Biogeochemistry **54:** 279-296. doi:10.1023/a:1010649227510

Sadro, S., and J. M. Melack. 2012. The effect of an extreme rain event on the biogeochemistry and ecosystem metabolism of an oligotrophic high-elevation lake. Arctic, Antarctic, and Alpine Research **44:** 222-231. doi:10.1657/1938-4246-44.2.222

Saidy, A. R., R. J. Smernik, J. A. Baldock, K. Kaiser, and J. Sanderman. 2013. The sorption of organic carbon onto differing clay minerals in the presence and absence of hydrous iron oxide. Geoderma **209–210:** 15-21. doi:10.1016/j.geoderma.2013.05.026

Scheffer, M., R. Portielje, and L. Zambrano. 2003. Fish facilitate wave resuspension of sediment. Limnology and Oceanography **48:** 1920-1926. doi:10.4319/lo.2003.48.5.1920

Scheffer, M., S. Rinaldi, A. Gragnani, L. R. Mur, and E. H. Vannes. 1997. On the dominance of filamentous cyanobacteria in shallow, turbid lakes. Ecology **78:** 272-282. doi

Shafer, M. M., J. T. Overdier, J. P. Hurley, D. Armstrong, and D. Webb. 1997. The influence of dissolved organic carbon, suspended particulates, and hydrology on the concentration, partitioning and variability of trace metals in two contrasting Wisconsin watersheds (U.S.A.). Chemical Geology **136:** 71-97. doi:10.1016/S0009-2541(96)00139-8

Shen, Y. H. 1999. Sorption of natural dissolved organic matter on soil. Chemosphere **38:** 1505-1515. doi:10.1016/s0045-6535(98)00371-3

Sillanpää, M. 2015. Chapter 1 - General introduction, p. 1-15. Natural Organic Matter in Water. Butterworth-Heinemann.

Sillanpää, M., A. Matilainen, and T. Lahtinen. 2015. Chapter 2 - Characterization of NOM, p. 17-53. Natural Organic Matter in Water. Butterworth-Heinemann.

Skoog, A. C., and V. A. Arias-Esquivel. 2009. The effect of induced anoxia and reoxygenation on benthic fluxes of organic carbon, phosphate, iron, and manganese. Science of The Total Environment **407:** 6085-6092. doi:10.1016/j.scitotenv.2009.08.030

Skrasner, S. W. and others 2006. Occurrence of a new generation of disinfection byproducts. Environmental Science & Technology **40:** 7175-7185. doi:10.1021/es060353j

Sleighter, R. L., P. Caricasole, K. M. Richards, T. Hanson, and P. G. Hatcher. 2015. Characterization of terrestrial dissolved organic matter fractionated by pH and polarity and their biological effects on plant growth. Chemical and Biological Technologies in Agriculture **2:** 1-19. doi:10.1186/s40538-015-0036-2

Sobek, S. and others 2009. Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. Limnology and Oceanography **54:** 2243-2254. doi:10.4319/lo.2009.54.6.2243

Sobek, S., L. J. Tranvik, and J. J. Cole. 2005. Temperature independence of carbon dioxide supersaturation in global lakes. Global Biogeochemical Cycles **19**. doi:10.1029/2004gb002264

Sodano, M., D. Said-Pullicino, A. F. Fiori, M. Catoni, M. Martin, and L. Celi. 2016. Sorption of paddy soil-derived dissolved organic matter on hydrous iron oxide-vermiculite mineral phases. Geoderma **261:** 169-177. doi:10.1016/j.geoderma.2015.07.014

Sondergaard, M., N. H. Borch, and B. Riemann. 2000. Dynamics of biodegradable DOC produced by freshwater plankton communities. Aquatic Microbial Ecology **23:** 73-83. doi:10.3354/ame023073

Søndergaard, M., E. Jeppesen, E. Mortensen, E. Dall, P. Kristensen, and O. Sortkjær. 1990. Phytoplankton biomass reduction after planktivorous fish reduction in a shallow, eutrophic lake: a combined effect of reduced internal P-loading and increased zooplankton grazing. Hydrobiologia **200-201:** 229-240. doi:10.1007/BF02530342

Søndergaard, M., P. Kristensen, and E. Jeppesen. 1992. Phosphorus release from resuspended sediment in the shallow and wind-exposed Lake Arresø, Denmark. Hydrobiologia **228:** 91-99. doi:10.1007/BF00006480

Sorichetti, R. J., I. F. Creed, and C. G. Trick. 2016. Iron and iron-binding ligands as cofactors that limit cyanobacterial biomass across a lake trophic gradient. Freshwater Biology **61:** 146-157. doi:10.1111/fwb.12689

Staehr, P. A., K. Sand-Jensen, A. L. Raun, B. Nilsson, and J. Kidmose. 2010. Drivers of metabolism and net heterotrophy in contrasting lakes. Limnology and Oceanography **55:** 817-830. doi:10.4319/lo.2009.55.2.0817

Steinberg, C. E. W. and others 2006. Dissolved humic substances – ecological driving forces from the individual to the ecosystem level? Freshwater Biology **51:** 1189-1210. doi:10.1111/j.1365-2427.2006.01571.x

Strzepek, R. F., K. A. Hunter, R. D. Frew, P. J. Harrison, and P. W. Boyd. 2012. Iron-light interactions differ in Southern Ocean phytoplankton. Limnology and Oceanography **57:** 1182-1200. doi:10.4319/lo.2012.57.4.1182

Stumm, W., and J. J. Morgen. 1996. Aquatic chemistry: chemical equilibria and rates in natural waters, Third ed.

Sucker, C., K. V. Wilpert, and H. Puhlmann. 2011. Acidification reversal in low mountain range streams of Germany. Environmental Monitoring and Assessment **174:** 65-89. doi:10.1007/s10661-010-1758-z

Taillefert, M., V. C. Hover, T. F. Rozan, S. M. Theberge, and G. W. Luther. 2002. The influence of sulfides on soluble organic-Fe(III) in anoxic sediment porewaters. Estuaries **25:** 1088-1096. doi:10.1007/BF02692206

Tammeorg, O., J. Niemisto, T. Mols, R. Laugaste, K. Panksep, and K. Kangur. 2013. Wind-induced sediment resuspension as a potential factor sustaining eutrophication in large and shallow Lake Peipsi. Aquatic Science **75:** 559-570. doi:10.1007/s00027-013-0300-0

Thayanukul, P., F. Kurisu, I. Kasuga, and H. Furumai. 2013. Evaluation of microbial regrowth potential by assimilable organic carbon in various reclaimed water and distribution systems. Water Research **47:** 225-232. doi:10.1016/j.watres.2012.09.051

Tipping, E. 1981. The adsorption of aquatic humic substances by iron oxides. Geochimica et Cosmochimica Acta **45:** 191-199. doi:10.1016/0016-7037(81)90162-9

Tittel, J., O. Buettner, K. Freier, A. Heiser, R. Sudbrack, and G. Ollesch. 2013. The age of terrestrial carbon export and rainfall intensity in a temperate river headwater system. Biogeochemistry **115:** 53-63. doi:10.1007/s10533-013-9896-3

Tittel, J., C. Müller, M. Schultze, A. Musolff, and K. Knöller. 2015. Fluvial radiocarbon and its temporal variability during contrasting hydrological conditions. Biogeochemistry **126:** 57-69. doi:10.1007/s10533-015-0137-9

Tranvik, L. J. and others 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnology and Oceanography **54:** 2298-2314. doi:10.4319/lo.2009.54.6_part_2.2298

Van Der Welle, M. E. W., M. Cuppens, L. P. M. Lamers, and J. G. M. Roelofs. 2006. Detoxifying toxicants: Interactions between sulfide and iron toxicity in freshwater wetlands. Environmental Toxicology and Chemistry **25:** 1592-1597. doi:10.1897/05-283R.1

Viollier, E. and others 2003. Benthic biogeochemistry: state of the art technologies and guidelines for the future of in situ survey. Journal of Experimental Marine Biology and Ecology **285–286:** 5-31. doi:10.1016/S0022-0981(02)00517-8

Von Wachenfeldt, E., and L. J. Tranvik. 2008. Sedimentation in boreal lakes - The role of flocculation of allochthonous dissolved organic matter in the water column. Ecosystems **11:** 803-814. doi:10.1007/s10021-008-9162-z

Vuorenmaa, J., M. Forsius, and J. Mannio. 2006. Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. Science of The Total Environment **365:** 47-65. doi:10.1016/j.scitotenv.2006.02.038

Wagai, R., and L. M. Mayer. 2007. Sorptive stabilization of organic matter in soils by hydrous iron oxides. Geochimica Et Cosmochimica Acta **71:** 25-35. doi:10.1016/j.gca.2006.08.047

Wauer, G., T. Gonsiorczyk, K. Kretschmer, P. Casper, and R. Koschel. 2005. Sediment treatment with a nitrate-storing compound to reduce phosphorus release. Water Research **39:** 494-500. doi:10.1016/j.watres.2004.10.017

Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, and K. Mopper. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental Science & Technology **37:** 4702-4708. doi:10.1021/es030360x

Wendt-Potthoff, K., C. Kloß, M. Schultze, and M. Koschorreck. 2014. Anaerobic metabolism of two hydro-morphological similar pre-dams under contrasting nutrient loading (Rappbode Reservoir System, Germany). International Review of Hydrobiology **99:** 350-362. doi:10.1002/iroh.201301673

Wetz, M. S., B. Hales, and P. A. Wheeler. 2008. Degradation of phytoplankton-derived organic matter: Implications for carbon and nitrogen biogeochemistry in coastal ecosystems. Estuarine, Coastal and Shelf Science **77:** 422-432. doi:10.1016/j.ecss.2007.10.002

Wetzel, R. 1992. Gradient-dominated ecosystems: sources and regulatory functions of dissolved organic matter in freshwater ecosystems. Hydrobiologia **229:** 181-198. doi:10.1007/BF00007000

Wetzel, R. G. 1995. Death, detritus, and energy-flow in aquatic ecosystems. Freshwater Biology **33:** 83-89. doi:10.1111/j.1365-2427.1995.tb00388.x

Williamson, C. E., R. S. Stemberger, D. P. Morris, T. M. Frost, and S. G. Paulsen. 1996. Ultraviolet radiation in North American lakes: Attenuation estimates from DOC measurements and implications for plankton communities. Limnology and Oceanography **41:** 1024-1034. doi:10.4319/lo.1996.41.5.1024

Wisser, D., S. Frolking, S. Hagen, and M. F. P. Bierkens. 2013. Beyond peak reservoir storage? A global estimate of declining water storage capacity in large reservoirs. Water Resources Research **49:** 5732-5739. doi:10.1002/wrcr.20452

Woods, G. C., M. J. Simpson, P. J. Koerner, A. Napoli, and A. J. Simpson. 2011. HILIC-NMR: Toward the identification of individual molecular components in dissolved organic matter. Environmental Science & Technology **45:** 3880-3886. doi:10.1021/es103425s

Yang, L., J. H. Choi, and J. Hur. 2014. Benthic flux of dissolved organic matter from lake sediment at different redox conditions and the possible effects of biogeochemical processes. Water Research **61:** 97-107. doi:10.1016/j.watres.2014.05.009

Zak, D., J. Gelbrecht, and C. E. W. Steinberg. 2004. Phosphorus retention at the redox interface of peatlands adjacent to surface waters in Northeast Germany. Biogeochemistry **70:** 357-368. doi:10.1007/s10533-003-0895-7

Zambrano, L., M. Scheffer, and M. Martínez-Ramos. 2001. Catastrophic response of lakes to benthivorous fish introduction. Oikos **94:** 344-350. doi:10.1034/j.1600-0706.2001.940215.x

Zarfl, C., A. E. Lumsdon, J. Berlekamp, L. Tydecks, and K. Tockner. 2015. A global boom in hydropower dam construction. Aquatic Science **77:** 161-170. doi:10.1007/s00027-014-0377-0

Zhang, M., C. Li, M. M. Benjamin, and Y. Chang. 2003. Fouling and natural organic matter removal in adsorbent/membrane systems for drinking water treatment. Environmental Science & Technology **37:** 1663-1669. doi:10.1021/es0260418

Zheng, Z., J. Lv, K. Lu, C. Jin, J. Zhu, and X. Liu. 2011. The impact of snail (Bellamya aeruginosa) bioturbation on sediment characteristics and organic carbon fluxes in an eutrophic pond. Clean-Soil Air Water **39:** 566-571. doi:10.1002/clen.201000212

Curriculum vitae

Tallent Dadi

Born, 13 July 1982 in Chiredzi, Zimbabwe

Education and research

Feb. 2013 to date	**PhD student**, Helmholtz Centre for Environmental Research – UFZ, Dept. of Lake Research, Magdeburg
Oct. 2010 to Dec 2012	**MSc in Environmental and Resource Management (Grade 1.5)**, Brandenburg University of Technology, Cottbus, Germany **Thesis title:** Interconnection between iron biogeochemistry and phosphorus release from sediments of a lake-river system (Lower Havel, Berlin)
Jan. 2007 - Jun. 2008.	**Postgraduate Diploma in Water and Sanitation**, Institute of Water and Sanitation, Zimbabwe
Aug. 2001 - Jul. 2004	**BSc Honours Degree in Applied Environmental Sciences**, University of Zimbabwe
Jan. 1999 – Dec. 2000	**Advanced Level (Mathematics, Biology and Chemistry),** Adventist High School, Gweru, Zimbabwe

Industrial experience

Dec. 2008 – Sept. 2010	ARIIFM LLC (United Arab Emirates, Abu Dhabi); *Facility management company;* Health Safety and Environment (HSE) Officer
Aug. 2004 – Dec. 2008	Metallon Gold Zimbabwe – Arcturus Mine (Harare, Zimbabwe); *Gold mining and processing company;* Safety Health and Environment (SHE) Officer

Publications

1. **Dadi, T.**, K. Friese, K. Wendt-Potthoff and M. Koschorreck. 2016. Benthic dissolved organic carbon fluxes in a drinking water reservoir. Limnol. Oceanogr.: Online. doi: 10.1002/lno.10224
2. **Dadi, T.**, C. Völkner, and M. Koschorreck. 2015. A sediment core incubation method to measure the flux of dissolved organic carbon between sediment and water. J. Soils Sediments: Online. doi: 10.1007/s11368-015-1213-4
3. Grüneberg, B., **T. Dadi**, C. Lindim, and H. Fischer. 2014. Effects of nitrogen and phosphorus load reduction on benthic phosphorus release in a riverine lake. Biogeochemistry 123: 185-202. doi: 10.1007/s10533-014-0062-3

Presentations

1. **Dadi T**, Wendt-Potthoff K, Friese K, Koschorreck M (2016). Role of the sediments for dissolved organic carbon (DOC) in lakes and reservoirs. EGU general assembly, Vienna, April 2016 (Poster)
2. **Dadi T**, Wendt-Potthoff K, Friese K, Koschorreck M (2015). Role of the sediments for dissolved organic carbon (DOC) in lakes and reservoirs. HIGRADE conference, 18 November 2015, Leipzig, (Poster)
3. Meyer M, **Dadi T** (2015). Algal Blooms in the North Sea. Utrecht Summer School, Utrecht, Netherlands, 6-17 July 2015 (Poster)
4. **Dadi T**, Wendt-Potthoff K, Friese K, Koschorreck M (2015). Benthic dissolved organic carbon (DOC) fluxes in drinking water reservoirs. ASLO conference, 22-27 February 2015, Granada, Spain, (Talk)
5. **Dadi T**, Wendt-Potthoff K, Friese K, Koschorreck M (2014). Benthic dissolved organic carbon (DOC) fluxes in a drinking water reservoir: Hassel pre-dam, Rappbode reservoir, Harz. DGL conference, 29Sept. – 02Oct. 2014, Magdeburg, Germany (Talk)

Professional affiliation

Association for the Sciences of Limnology and Oceanography (ASLO) member

Scholarship awards

Katholischer Akademischer Ausländer-Dienst (KAAD) Scholar (2011 to 2012)

Erklärung über den persöhnlichen Anteil an den Publikationen

Study 1 (Chapter 3):

Dadi T, Völkner C, Koschorreck M (2015). A sediment core incubation method to measure the flux of dissolved organic carbon between sediment and water. J Soil Sediment 15:2350-2358. doi:10.1007/s11368-015-1213-4

Design and data collection: *Tallent Dadi (60%),* Corinna Völkner (10%), Matthias Koschorreck (30%)

Data analysis: *Tallent Dadi (100%)*

Writing: *Tallent Dadi (80%),* Matthias Koschorreck (20%)

Study 2 (Chapter 4a):

Dadi, T., K. Friese, K. Wendt-Potthoff, and M. Koschorreck. 2016. Benthic dissolved organic carbon fluxes in a drinking water reservoir. Limnol. Oceanogr.: 445-459. doi:doi:10.1002/lno.10224

Design and data collection: *Tallent Dadi (70%)*, Kurt Friese (10%), Matthias Koschorreck (20%)

Data analysis: *Tallent Dadi (100%)*

Writing: *Tallent Dadi (70%),* Kurt Friese(10%), Katrin Wendt-Potthoff (10%), Matthias Koschorreck (10%)

Study 3 (Chapter 5):

Dadi, T., K. Wendt-Potthoff, and M. Koschorreck. Sediment resuspension effects on dissolved organic carbon fluxes and microbial metabolic potentials in reservoirs. (Manuscript under review)

Design and data collection: *Tallent Dadi (70%)*, Katrin Wendt-Potthoff (10%), Matthias Koschorreck (20%)

Data analysis: *Tallent Dadi (100%)*

Writing: *Tallent Dadi (80%)*, Katrin Wendt-Potthoff (10%), Matthias Koschorreck (10%)

Tallent Dadi

Prof. Dr. Kurt Friese

Eidesstattliche Erklärung / Declaration under Oath

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