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Key Points:

- Anoxia induces DOC diffusion from lake sediments
- Anoxic DOC diffusion is quantitatively comparable to sediment mineralization and OC burial
- Anoxic DOC diffusion can be relevant for sediment C budgets

Supporting Information:

- Supporting Information S1

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Enhanced carbon loss from anoxic lake sediment through diffusion of dissolved organic carbon

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Abstract Lakes are highly relevant players in the global carbon cycle as they can store large amounts of organic carbon (OC) in sediments, thereby removing OC from the actively cycling pool. However, sediment OC can be released to pore water under anoxic conditions and diffuse into the water column. In carbon budgets of lake ecosystems, this potential OC loss pathway from sediments is generally disregarded. Combining field observations and incubation experiments, we quantitatively investigated dissolved OC (DOC) diffusion from sediments into anoxic water of a boreal lake. We observed substantial increases of bottom water DOC (26% in situ, 16% incubation), translating into a DOC flux from the sediment that was comparable to anoxic sediment respiration (3.3 versus 5.1 mmol m⁻² d⁻¹). Optical characterization indicated that colored and aromatic DOC was preferentially released. Reactivity assays showed that DOC released from anoxic sediment enhanced water column respiration and flocculation in reoxygenated water. Upon water oxygenation, flocculation was the most important loss pathway removing ~77% of released DOC, but the remaining ~23% was mineralized, constituting a pathway of permanent loss of sediment OC. DOC diffusion from lake sediment during anoxia and subsequent mineralization in oxic water during mixing increases overall OC loss from anoxic sediments by ~15%. This study enlarges our understanding of lake ecosystems by showing that under anoxic conditions significant amounts of DOC can be released from OC stored in sediments and enter the active aquatic carbon cycle again.

1. Introduction

Freshwater systems play an important role in the global carbon cycle by connecting the organic carbon (OC) cycles of the terrestrial and the marine realm, whereby about half of the OC entering freshwater systems is stored or released as gas to the atmosphere [Cole *et al.*, 2007]. Lakes are specifically significant, as they can store large amounts of OC in the sediments and thereby exclude OC from the actively cycling OC pool [Cole *et al.*, 2007]. In sediments, OC is either buried, thereby representing an important global C sink, or it is mineralized and diffuses out of the sediments as carbon dioxide or methane [Sobek *et al.*, 2009]. In addition, solid-phase sediment OC can be released to pore water under anoxic conditions and diffuse as dissolved organic carbon (DOC) out of the sediment [O'loughlin and Chin, 2004; Skoog and Arias-Esquivel, 2009]. However, in lakes, the relevance of this DOC diffusion from anoxic sediments has not been studied yet, even though it might affect the carbon sink function of lake sediments.

Various factors, e.g., sediment OC composition and oxygen exposure time, contribute to the stabilization and preservation of OC in sediments [Hedges *et al.*, 1999; Sobek *et al.*, 2009]. Furthermore, it was reported that the presence of Fe(III) contributes to the sedimentation and burial of OC by sorption and aggregation of iron-(hydroxy)oxides with DOC [Lalonde *et al.*, 2012; Tipping and Woof, 1983]. This aggregation contributes to the preservation of OC by preventing it from microbial degradation [Boudot, 1989; Jones and Edwards, 1998; Keil *et al.*, 1994]. Lalonde *et al.* [2012] estimated that ~20% of OC in sediments is directly bound to the reactive iron phase and constitutes a "rusty sink" of OC. Recent studies in marine sediments and ground-water indicate that iron-bound OC can be mobilized under anoxic conditions and diffuse from the sediment into the water column [Mladenov *et al.*, 2009; Skoog *et al.*, 1996; Skoog and Arias-Esquivel, 2009]. Under anoxic conditions, reductive dissolution of Fe(III) releases Fe(II) and previously bound OC, leading to coaccumulation of Fe(II) and DOC in the sediment pore water [O'loughlin and Chin, 2004]. During oxic conditions in the water column, the upper sediment layers are oxygenated and iron is present as Fe(III), efficiently trapping DOC and preventing its diffusion from sediments into the water column. If bottom water turns anoxic, DOC will no longer be trapped and can diffuse freely into bottom water, as was shown in marine sediment incubations [Skoog and Arias-Esquivel, 2009].

It is likely that this process is also prevalent in freshwater sediments, since freshwaters have generally high contents of both Fe and OC [Cole *et al.*, 2007; Kritzberg *et al.*, 2014; Köhler *et al.*, 2013]. In freshwaters, especially in the boreal zone, DOC concentration was found to be coupled to iron cycling in surface water [Kritzberg and Ekström, 2012; Tipping and Woof, 1983; Weyhenmeyer *et al.*, 2014] and to coaccumulate in sediment pore water [O'loughlin and Chin, 2004]. Terrestrial-derived humic OC compounds are known to be preferentially sorbed to Fe(III) [Kaiser and Guggenberger, 2000; Riedel *et al.*, 2013] and released again under anoxic conditions in wetlands and marine systems [Chin *et al.*, 1998; Skoog *et al.*, 1996]. Accordingly, reductive dissolution of Fe(III) in soils releases DOC and Fe(II) into the soil pore water and further into surface waters [Knorr, 2013]. In particular, boreal aquatic systems are high in terrestrial humic OC [Sobek *et al.*, 2007; Thurman, 1985], and the carbon cycling is tightly coupled to cycling of Fe [Kritzberg and Ekström, 2012; Köhler *et al.*, 2013; Weyhenmeyer *et al.*, 2014], thus these systems are potentially very sensitive for iron-DOC interactions. Iron reduction in anoxic lake sediments has been repeatedly shown to be important for the release and cycling of other compounds like phosphate [Li *et al.*, 2012] and arsenic [Smedley and Kinniburgh, 2013]. Nevertheless, DOC release from anoxic sediments has never been systematically studied in lakes, despite evidence of DOC diffusion from sediment already at hypoxic ($1\text{--}2\text{ mg O}_2\text{ L}^{-1}$) conditions [Yang *et al.*, 2014].

While the quantity of DOC diffusing from anoxic lake sediment is of interest, also the reactivity of any DOC released from the sediment is important. Through sorption to iron, bioavailable OC can be preserved from degradation and, after being released from iron, become accessible for microbial consumption [Boudot, 1989; Jones and Edwards, 1998; Lalonde *et al.*, 2012]. Whether the DOC released from sediment will be respired or sorb again to Fe(III) and precipitate upon oxygenation will be largely defined by its bioavailability, i.e., how fast the DOC will be mineralized. At present, knowledge on the reactivity of sediment released DOC is lacking, even though this would help constrain the importance of DOC diffusion from anoxic sediments as a pathway of OC loss from the sediment.

In this study, we quantified DOC diffusion from sediment into anoxic water and the subsequent fate of the diffusing DOC in the water column for a hemiboreal lake in south-west Sweden. We hypothesized that in the studied lake DOC will diffuse from sediment pore water into anoxic bottom water, and that part of this DOC is bioavailable and therefore will be mineralized when released into the water column. To test this hypothesis, we conducted field observations, incubation experiments of sediment cores under oxic and anoxic conditions, and reactivity assays of DOC retrieved from the sediment incubations. We also used a diffusion model to identify whether the rate-limiting step for DOC diffusion from sediment is DOC dissolution from the sediment or diffusion from pore water into the water column.

2. Materials and Methods

2.1. Study Site

Lake Erssjön in southwestern Sweden ($58^{\circ}22'\text{N}$, $12^{\circ}10'\text{E}$) is a small (6.2 ha) hemiboreal lake with a maximal depth of $\sim 4.5\text{ m}$ [Rydin *et al.*, 1999]. The lake is dystrophic with high DOC concentration ($0.8\text{--}2.5\text{ mmol L}^{-1}$), high humic content, and brown color of the water (specific ultraviolet absorbance (SUVA) = $3.9\text{--}5.5\text{ L mg C}^{-1}\text{ m}^{-1}$ and decadic absorbance coefficient $\alpha_{420} = 0.05\text{--}0.21\text{ cm}^{-1}$), based on biweekly samples from spring to autumn for monitoring period 2012–2013 (data not shown). Decadic absorbance coefficient α at 420 nm was derived by normalizing the dimensionless absorbance measure with path length cm^{-1} [Hu *et al.*, 2002]. SUVA was used as a proxy for aromaticity and was determined by dividing the decadic absorbance coefficient (normalized to a path length of m^{-1}) at 254 with the DOC concentration [Weishaar *et al.*, 2003]. Total phosphorus and nitrogen concentrations range from 0.7 to $2.8\text{ }\mu\text{mol L}^{-1}$ and from 48 to $253\text{ }\mu\text{mol L}^{-1}$, respectively, but most of it is organically bound. The catchment (750 ha) is mainly covered by coniferous forest (Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*)), a minor share of peat and agricultural land underlined by granite bedrock with a thin soil layer. Shallow lakes with high DOC concentrations are typical for this region (average of maximum depth of 6266 monitored Swedish lakes: $11 \pm 8.4\text{ m}$ and mean and max DOC concentration of 16,889 measurements in 6266 Swedish lakes ($0.8 \pm 0.4\text{ mmol L}^{-1}$ and 3.8 mmol L^{-1} , respectively; <http://miljodata.slu.se/mvm/>)), given the flat topography of the land and the high input of terrestrial organic carbon [Sobek *et al.*, 2011]. The brown color of the water and the wind protection by surrounding forest generally leads to the development of stable summer

Figure 1. Schematic overview of the setup of the sediment core incubations and subsequent DOC reactivity assays in bottles, showing the different oxygen treatments. Intact sediment cores were incubated for 24 days under oxic, anoxic, and anoxic-oxic conditions. The cores for the anoxic-oxic treatment were anoxic for 17 days and were subsequently oxygenated for the remaining time of the incubation. Water for the DOC reactivity assay was retrieved from sediment incubations at day 17 and incubated for 40 days. O-O and A-O represent water samples incubated under oxic conditions with water originating from oxic and anoxic sediment incubations, respectively. O-A and A-A represent water samples incubated under anoxic conditions with water originating from oxic and anoxic sediment incubations, respectively.

(11 June, 9 July, and 14 August 2014), and after stratification (27 August). Sample water for DOC, dissolved organic matter (DOM) absorbance, and Fe determination was immediately filtered (GF/F) on site. In the case of anoxic sample water, water was filled air free in a 50 mL syringe and directly filtered into a ferrozine solution to fix Fe(II) (see below). To test for potential color loss of the ferrozine-Fe complex over the time until analysis, additional filtered water was kept untreated for later total Fe analysis in the laboratory. No fixation was added to oxic water samples since both, the fixation by ferrozine and HCl (in a final concentration of 0.01 mol L^{-1}), were found in preliminary tests to reduce Fe(III) in oxic sample water ($22 \pm 5\%$ for ferrozine fixation and $40 \pm 11\%$ for HCl fixation in oxic sample water) ($\pm$ indicating 1 standard deviation). Temperature, O_2 , and pH data were measured with a YSI six-series multiparameter sonde. Between sampling campaigns, the YSI sonde was installed at 0.5 m depth above the sediment (3.7–4.4 m from surface) to monitor O_2 , specific conductivity, temperature, and pH in the hypolimnion at a measurement frequency of 2 h. In addition, seven temperature loggers (Onset HOBO Pro V2) were permanently installed at depth intervals of 0.5 m and measured temperature every 2 h. Precipitation data were obtained from the meteorological station in Uddevalla, about 8 km from Lake Erssjön (Swedish Meteorological and Hydrological Institute, www.smhi.se).

2.3. Sediment Incubation Setup and Sampling

Three different treatments were applied for the sediment incubations (Figure 1): (i) anoxic incubations with the sediment and the overlaying water being anoxic, (ii) oxic incubations with oxic water overlaying the sediment, causing also the surface sediment layer (upper 2–3 mm, see section 3) to be oxic during the incubations, and (iii) anoxic-oxic incubations where incubations started with anoxic water that was oxygenated during the last part of the incubation.

stratification even in shallow lakes [Fee *et al.*, 1996]. Lake Erssjön and its catchment are intensively monitored within the framework of a multidisciplinary project, which aims to integrate greenhouse gas emissions from aquatic and terrestrial systems into the landscape-scale budget [Klemedtsson, 2012].

2.2. Sampling

Intact sediment cores were obtained from the deepest point ($\sim 4.5 \text{ m}$) in Lake Erssjön with a UWITEC sediment corer on 1 February 2014 during ice cover and stored at 4°C until start of incubation experiments (4 weeks). The water column at that time point was weakly stratified below 1 m, and bottom water was oxic ($231 \mu\text{mol O}_2 \text{ L}^{-1}$). DOC and total Fe concentrations in the bottom water during time of sampling were 1.9 mmol L^{-1} and $10.8 \mu\text{mol L}^{-1}$, respectively. Bottom water temperature was 3.9°C . Ten liter bottom water for the core incubation experiment was collected with a Ruttner water sampler.

During spring to autumn 2014, the water column was sampled using a Ruttner water sampler at the deepest point of the lake at 0.5, 2, 3.5, 4, and 4.5 m depth before (23 May), during

The top 10 cm (255 cm³) of 12 sediment cores was transferred as intact cores, i.e., without visible disturbance of sediment structures, together with the overlaying water from the sampling tubes into transparent unplasticized polyvinyl chloride (500 × 57 mm, 6 mm wall thickness) tubes and additionally filled to 765 cm³ with lake bottom water [Gudas et al., 2015]. The tubes were sealed from the bottom (and later from the top) with stoppers holding three layers of O rings. This setting was previously extensively tested and kept the diffusion of oxygen over the plastic walls into the core at nondetectable levels, making it possible to maintain anoxic conditions throughout the experiment. The cores were kept in temperature controlled water baths at 10°C, close to in situ bottom water temperature in Erssjön during summer stratification. Inside the cores a floating stirring device, agitated by a rotating magnet in the water bath outside the sediment cores, assured continuous mixing of the water column.

After the sediment cores and the overlaying lake water were allowed to adjust to incubation temperature and oxic condition for 1 week, water of eight cores was flushed with N₂ to reach low O₂ concentrations and immediately closed before taking the first samples. The cores were all below 15 μmol O₂ L⁻¹ during the first sampling and completely anoxic at the next sampling after 3 days. Oxygen saturation was measured using optode sensor spots (model PSt3, PreSens, Precision Sensing). Overlaying water from the sediment cores was sampled by pushing the top stopper downward, forcing water to flow out through a Tygon tube connected to the stopper's outlet. From there water for DOC and Fe analyses was collected oxygen free in N₂-flushed 50 mL syringes, which were attached to the Tygon tube by a luer lock valve. pH was instantly determined after sampling on a mobile pH meter (Metrohm). Dissolved inorganic carbon (DIC) samples were directly filled bubble free from the Tygon tube in a 17 mL glass vial and closed headspace free. Ten milliliters of water was equilibrated in the sampling syringe for 1 min with 7 mL of N₂, and headspace was analyzed within the same day for CH₄ concentration. Samples for DOC and Fe from the anoxic cores were immediately transferred for anoxic GF/F filtration into the N₂ atmosphere of a glove box (BELLE) with constant monitoring of O₂ concentration to guarantee anoxic conditions. Fe fixation with ferrozine was started in the glove box immediately after filtration. For the oxic incubations, the remaining four cores were incubated open, allowing constant oxygen saturation, and sampled with a Tygon tube connected to a 50 mL syringe. Samples were taken every 3 to 4 days for a total of 24 days. On day 17 a subset of four anoxic cores was opened and allowed to become oxygenated for the rest of the incubation. On the same day an additional 100 mL water was sampled from four oxic and four anoxic cores for the DOC reactivity assay (see below).

Areal DOC and Fe fluxes (mol m⁻² d⁻¹) from sediment into the overlaying water were calculated by multiplying per day concentration difference (mol m⁻³ d⁻¹) between samplings with the height of the water in the incubation tubes (m). Accordingly, anoxic sediment respiration rates were calculated from DIC and CH₄ measurements between sampling day 0–11 and 11–17 [Gudas et al., 2015]. Oxic sediment respiration rates were determined before starting the incubation experiment (i.e., day -3 to 0) by closing the oxic cores and measuring DIC increase over 3 days. Oxygen concentration dropped by 43 ± 3% during that time, and hence, the water did not turn anoxic during oxic incubations. Using O₂ consumption rates (mmol m⁻² d⁻¹) during the oxic respiration measurements, sediment porosity (0.93 [Broman, 2013]), and molecular diffusivity, O₂ penetration depth into the sediment for the oxic sediment incubation was calculated, assuming a linear concentration gradient [Hartnett et al., 1998].

At the end of sediment incubations, the cores were sliced in 1 or 2 cm thick slices in the N₂ environment of a glove box. The sediment was centrifuged (30 min, 2000 rpm, 4°C) prior to GF/F filtration, and the pore water was analyzed for DOC concentration. Sediments were freeze dried and homogenized for analysis of OC content.

2.4. DOC Reactivity Assay

After 17 days of sediment incubation, overlaying water from anoxic and oxic cores was collected to assess the fate of the released DOC, by measuring mineralization (CO₂ and CH₄ production) and formation of particulate OC (POC) over time. Overlaying water from the sediment incubations was collected as soon as a clear DOC concentration increase was detected. Water incubations were run under oxic and anoxic conditions to test the effect of the changing redox conditions on the fate of the DOC. One hundred milliliters of sediment overlaying water collected from each core was filtered through GF/F filters and then split up in two 50 mL samples that were incubated at room temperature in the dark in 120 mL crimp-seal vials closed with thick butyl rubber

stoppers. For the water derived from anoxic sediment incubations, one vial was allowed to become oxic by shaking it with air headspace (A-O) and the other vial was kept anoxic in the glove box (A-A). The reverse was done for the water samples from oxic sediment cores, one was kept oxic (O-O) while the other one was flushed with N₂ to establish anoxia (O-A). Over a time period of 40 days, headspace was sampled every week or every other week for CO₂ and CH₄ concentrations and oxygen concentration was measured using micro-optodes (model PSt3, PreSens, Precision Sensing). Before taking gas headspace samples, overpressure in the vials was created to prevent potential air intrusion into the vials during sampling of underpressurized vials. Seven milliliters of N₂ was added to the vials, shaken for 2 min, and 7 mL was retrieved again in the same syringe. Before and after adding the N₂ gas, pressure inside the vials was monitored by inserting a needle attached to a manometer to account for the dilution by the added gas. At the end of incubation, water was filtered (GF/F, combusted) and analyzed for DOC concentration. The filters were kept to measure POC concentration. DOC loss during the reactivity is reported as the sum of CO₂ production and POC formation, providing analytically more robust information about DOC loss than direct measurements of DOC concentration changes, because in the anoxic water incubations (A-A and O-A) changes in DOC concentrations were small compared to the high DOC concentration and within the analytical error of the analysis (Figure S1 in the supporting information). Nevertheless, DOC concentration decrease correlated well with CO₂ and POC formation (Pearson correlation: $r = 0.98$, $p < 0.01$). CH₄ concentrations were throughout the DOC reactivity assay very low and did not contribute to DOC mineralization (maximal CH₄ concentration was 1.8 $\mu\text{mol L}^{-1}$, and maximal change in CH₄ concentration during the whole incubation was 0.6 $\mu\text{mol L}^{-1} \text{ d}^{-1}$) and were therefore not included in the results.

2.5. Chemical and Optical Analyses

DIC and DOC concentrations were measured on a Sievers 900 total organic carbon analyzer with a precision of the analytical method of $< 1\%$ relative standard deviation and an accuracy of $\pm 2\%$ or ± 0.5 ppb, whichever is greater. CH₄ (and CO₂ in the DOC reactivity assay) was measured on a gas chromatograph equipped with a flame ionization detector and a nickel catalyst for converting CO₂ in the column effluent to CH₄ (Agilent Technologies, 7890A GC System). From headspace sampling, CH₄ and CO₂ concentrations in the water were calculated with the gas law and the Bunsen solubility coefficient for CH₄ and CO₂, respectively [Weiss, 1974; Yamamoto *et al.*, 1976]. In the DOC reactivity assays, we wanted to accomplish several measurements over time in spite of limited water volume and, therefore, chose to measure the change of CO₂ and CH₄ in the headspace of closed vials. Since this approach did not allow measuring pH over time we estimated pH (Figure S2) based on the linear relationship between CO₂ concentration and pH in the sediment incubations ($\text{pH} = -0.0028 [\text{CO}_2] + 6.9468$, $R^2 = 0.764$, $p < 0.001$). DIC concentration increase in the DOC reactivity assays, calculated from estimated pH and measured CO₂, exceeded CO₂ concentration increase for all treatments, but the differences between treatments were not affected by choosing either CO₂ or DIC as a measure of mineralization (see supporting information, Figure S1). We report the measured CO₂ concentration increase instead of the calculated DIC concentrations for the DOC reactivity assay, because calculation of DIC is based on estimated pH, and because CO₂-derived mineralization rates were smaller than DIC-derived mineralization rates; thus, making our conclusions on the reactivity of DOC released from sediment conservative.

For Fe(II) and Fe(III) measurements by means of the ferrozine method, the protocol by Viollier *et al.* [2000] was adjusted by using 0.15 mol L^{-1} ascorbic acid as a reducing agent and allowing the reduction reaction to take place overnight. No additional buffer is needed following this adjusted method. Since samples were immediately measured after adding the ferrozine solution (except anoxic field samples, see above), potential autoreduction was negligible [Verschoor and Molot, 2013]. No iron contamination through sample handling (filtration) could be detected in blank samples prepared with iron-free artificial lake water (mean Fe total = $0.1 \pm 0.2 \mu\text{mol L}^{-1}$, $n = 40$). Absorbance was recorded on a spectrophotometer (Perkin Elmer, Waltham, USA) at 562 nm. POC was determined on precombusted (450°C) GF/F filters and sediment OC content on freeze dried sediments, both combusted in an elemental analyzer (NA 1500, Carlo Erba instruments).

DOM absorbance spectra were measured on GF/F filtered water in a 0.5 cm quartz cuvette from 200 to 600 nm at 1 nm intervals using a Lambda 40 UV-visible spectrophotometer (Perkin Elmer, Waltham, USA). Absorbance coefficients are reported in decadic form (normalized to path length cm^{-1}) [Hu *et al.*, 2002]. Since Fe(III) significantly contributes to total absorbance [Poulin *et al.*, 2014; Weishaar *et al.*, 2003], we

corrected for the absorbance of Fe(III) in order to derive DOM absorbance independent of Fe(III) concentration. We investigated the effect of Fe(III) on DOM absorbance by (i) adding Fe(III) spikes ($10\text{--}90\ \mu\text{mol L}^{-1}$) to separate Lake Erssjön water samples with low Fe(III) concentrations while keeping pH constant and (ii) by oxidizing anoxic water from sediment incubations with high Fe(II) concentrations and comparing absorbance under anoxic conditions (no Fe(III)) and oxic conditions (all or part of Fe(II) oxidized to Fe(III)). The positive linear relationship between Fe(III) concentration and absorbance was used to correct absorbance data for specific wavelengths (Fe absorbance correction factors ($\text{L } \mu\text{mol}^{-1} \text{ Fe } 0.5\ \text{cm}^{-1}$) for 420 nm: slope: 0.000343, intercept: 0.00381, $R^2 = 0.676$, $p < 0.001$; for 365 nm: slope: 0.000818, intercept: 0.00137, $R^2 = 0.865$, $p < 0.001$; for 254 nm: slope: 0.00196, intercept: 0.000380, $R^2 = 0.937$, $p < 0.001$; for 250 nm: slope: 0.00201, intercept: 0.0003234, $R^2 = 0.935$, $p < 0.001$). Because Fe(II) may have been oxidized during sample storage (maximal 2 days at 4°C) and handling during absorbance measurements, we tested how much Fe(II) was oxidized until the time of absorbance measurements and used these results to account for the amount of Fe(III) in the samples at time of absorbance measurements. After 1 day, Fe(II) in the originally anoxic samples still accounted for $48 \pm 16\%$ of total Fe and decreased to $10 \pm 14\%$ after 2 days.

2.6. DOC Diffusion Model

We used a diffusion model to simulate the change in DOC concentration in overlaying water in the sediment incubation experiments to (i) discern the rate-limiting step for DOC fluxes from the sediment into the water column (DOC dissolution versus diffusion) and (ii) to test the effect of different overlaying water volumes on DOC diffusion fluxes because with the chosen sediment incubation setup, concentration changes and associated fluxes from the sediment into the overlaying water were affected by the decreasing volume during sample retrieval. Decreasing volume of overlaying water resulted in DOC concentrations increasing more rapidly than if there were a larger volume receiving the DOC diffusing from the sediment. This, in turn, slows down the diffusion rates. In this respect, a sampling effect on the concentration gradient between sediment pore water and overlaying water was unavoidable. Even if we had replaced the sampled water to maintain a constant water volume during the incubation, concentrations in the water would have changed and affected diffusion rates.

We first simulated the change in DOC concentration in overlaying water at the time steps of the incubation experiment based on diffusion being the only rate limiting step, i.e., pore water concentrations were assumed to stay constant. To disentangle the effect of the changing volumes on the diffusion flux and DOC concentration, we then used this diffusion model to simulate the effect of a constant volume of the overlaying water on DOC concentration change. To estimate DOC concentration increase in the water above the sediment, we used Fick's first law of diffusion [Berner *et al.*, 1980; Boudreau, 1997]:

$$F = k (C_{\text{sed}} - C) = (\delta M / \delta t) / A \quad (1)$$

where F ($\text{mol m}^{-2} \text{d}^{-1}$) is the DOC flux across the sediment water interface and $k = D/z$, where D ($\text{cm}^2 \text{s}^{-1}$) is the free diffusion coefficient for DOM and z (m) is the thickness of the diffusive boundary layer. C_{sed} (mol L^{-1}) is the DOC concentration in the pore water of the upper sediment layer, C (mol L^{-1}) the concentration in the overlaying water, M (mol) the amount of DOC in the overlaying water, and A (m^2) the sediment surface area. Since $M = A h C$, where h (m) stands for the water height in the incubation tubes, the concentration increase with time (t) can be derived from formula (1):

$$C(t) = C_{\text{sed}} - (C_{\text{sed}} - C_0) / (\exp((k/h) (t - t_0))) \quad (2)$$

Since D is dependent on the molecular weight of the solute, we used a range of D values ($1\text{--}1.7 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) according to molecular weights from 1 to 10 kDa as reported by Burdige *et al.* [1992]. For concentration in the pore water, C_{sed} , the measured concentration in the sediment pore water at the end of the experiment was used ($2.45 \pm 0.01 \text{ mmol L}^{-1}$, excluding one extreme outlier of 4.6 mmol L^{-1}) and assumed to be constant over the course of the experiment. This assumption is supported by the similarity of pore water DOC concentration over sediment depth in anoxic sediment layers (see section 3), indicating that DOC diffusion to overlaying water does not result in a depletion of DOC in the most surficial sediment layers. For C_0 , the starting concentration for the first time interval of the incubation, the starting concentration in the incubations ($1.98 \pm 0.04 \text{ mol L}^{-1}$) was used and for each progressing time interval the newly calculated $C(t)$ was used as input variable for C_0 . For z , the previously reported ranges for sediment diffusive boundary layer thickness

[Brand *et al.*, 2009 (0.16–0.84 mm)] were used and adjusted (0.3–0.7 mm) for best fit with experimental data. The water height (h) of the incubation was the average from the incubation replicates for each time interval but was set to constant values when modeling flux into a constant volume. To account for the uncertainties of input variables, we run Monte Carlo simulations with 10^5 iterations on Matlab (R2013b, 8.2.0 701, The MathWorks) for mean and error estimations.

2.7. Data Treatment

For analysis of incubation data (DOC and total Fe concentrations and absorbance parameters), linear mixed effects (lme) models were used where explanatory variables are included as either fixed (influencing the mean of the response variable) or random (influencing its variance) effect using the software R (version 3.1.1) [Crawley, 2007]. The basic model included incubation O_2 conditions (anoxic or oxic) as fixed effect and the core replicates and time as random effects. Model extensions were tested for (i) a variance function which allows different variances of the response variable per level of the fixed effect, and/or (ii) a first-order temporal autoregressive process, which assumes that correlation between measurements decreases with increasing time distance. If this improved the relative goodness of the model fit, the model was included in the basic model described above. The models were checked using diagnostic residual plots, and the significance of the fixed effect was assessed by analysis of variance [Crawley, 2007]. If necessary, data were log transformed to approach normal distribution. To confirm the robustness of the statistical test, and in cases when the lme models were too complex to converge (absorbance data), data were tested with lme models using averaged values, thereby excluding the replicates as random effects, and additionally with multivariate repeated measures analysis of variance (rMANOVA) using O_2 conditions and time as explanatory variables [Gueorguieva and Krystal, 2004]. When analyzing only start and end points of incubations, e.g., for DOC reactivity assay, the different treatments were compared by repeated measures rMANOVA only, using time and the origin of the DOC as explanatory variables. Simultaneous inference procedures were used to adjust for multiplicity, and corrected p values are reported [Hothorn *et al.*, 2008]. Generally, results are reported as mean values ± 1 standard deviation.

3. Results

3.1. Lake In Situ Measurements

The lake started to establish a stable thermal stratification after the sampling campaign of 23 May, and the hypolimnion turned anoxic after 11 June and remained so until 19 August at ~ 1 m above the lake bottom at the deepest point in the lake (Figures 2, 3, and S3). Three sampling occasions covered anoxic conditions in the hypolimnion: 11 June, 9 July, and 14 August. Between 23 May and 11 June, while the hypolimnion still contained oxygen (Figure 2), no change in hypolimnetic concentrations of DOC or Fe could be observed (Figure 3). After the onset of anoxia, DOC concentrations in the hypolimnion increased by $400 \mu\text{mol L}^{-1}$ (26% increase) (Figure 3) translating into a DOC flux of $4.7 \pm 0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ for the entire anoxic period (accounting for depth of the thermocline and lake bathymetry returned a weighted mean of the hypolimnion depth of 0.67 m). If calculated separately for the two anoxic periods bracketed by the three sampling occasions (11 June to 9 July and 9 July to 14 August), DOC fluxes were very similar (5.0 and $4.4 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively). Hypolimnetic total Fe concentration during the period of 11 June to 14 August increased by $67 \mu\text{mol L}^{-1}$ (480% increase) leading to a calculated flux of total Fe of $736 \pm 282 \mu\text{mol m}^{-2} \text{ d}^{-1}$. Fe(II) accounted for $92 \pm 2\%$ of total Fe concentration on 9 July and for $99 \pm 2\%$ on 14 August. At the sampling campaign of 14 August, increased DOC concentrations were observed also in the epilimnion (Figure 3), related to precipitation in the catchment (Figure 2). High DOC concentrations persisted also after the lake had mixed on 19 August, resulting in vertically homogeneous high DOC concentrations (Figure 3).

3.2. DOC and Iron Diffusion From Incubated Sediments

In the anoxic sediment incubations, DOC and total Fe concentrations in the overlaying water increased during the incubation by $316 \pm 77.6 \mu\text{mol L}^{-1}$ (16% increase) and $41.1 \pm 10.2 \mu\text{mol L}^{-1}$ (282% increase), respectively, and were significantly correlated (Spearman's rank correlation: $\rho = 0.86$; $p < 0.001$) (Figure 4). The contribution of Fe(II) to total Fe increased with rising total Fe concentrations in the anoxic incubations. When total Fe was above $40 \mu\text{mol L}^{-1}$, 90–100% of it was detected as Fe(II). But only at the last sampling occasion, all iron was completely ($>99\%$) reduced. In contrast, in the oxic treatments, DOC concentration

Figure 2. (a) Daily precipitation measured at the metrological station Uddevalla, 8 km from Lake Erssjön, during summer stratification period in 2014. (b) Oxygen concentration and specific conductivity in the hypolimnion (0.5 m above sediment) and (c) temperature depth profile over the same time period in Lake Erssjön. Vertical gray bars indicate sampling occasions for O₂, DOC, and iron concentrations.

decreased by $296 \pm 43.4 \mu\text{mol L}^{-1}$ (15.3% decrease) and total Fe concentrations weakly followed the decreasing DOC concentrations ($\rho = 0.56$; $p = 0.001$), but the coupling between DOC and Fe concentrations was less pronounced than in the anoxic incubations. Linear mixed models revealed that DOC and total Fe concentrations in oxic and anoxic treatments were significantly different after day 3 (lme for DOC: $p = 0.0103$ and for total Fe: $p < 0.001$, respectively). As long as the anoxic-oxic treatment remained anoxic (day 17), there was no statistically significant difference to the anoxic treatment (average concentration lme model: $p = 0.0663$ for DOC and $p = 0.0984$ for total Fe concentrations). After exposing anoxic-oxic treatment cores to oxygen

Figure 3. (a) Oxygen, (b) specific conductivity, (c) total Fe and (d) DOC concentration profiles in Lake Erssjön during summer stratification 2014.

Figure 4. Mean concentration changes of (a) DOC and (b) total Fe in the water above the sediment during incubations under different oxygen conditions. At day 17 (indicated by the dashed line), the anoxic-oxic incubations were opened and oxygenated. Error bars indicate standard deviations ($n = 4$).

on day 17, both Fe and DOC concentrations dropped rapidly and were after 7 days back to the levels at the experiment start, and were significantly different from the continuously anoxic incubations (rMANOVA: $p = 0.022$ for DOC and $p < 0.001$ for total Fe concentration).

Increasing DOC and Fe concentrations were observed after day 3 of the anoxic incubation, with highest DOC diffusion fluxes at days 7 and 14 (12 ± 4.9 and $4.6 \pm 3.1 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively) and highest total Fe diffusion fluxes at days 7 and 11 (900 ± 405 and $1007 \pm 329 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$, respectively) (Figure 4 and Table 1). There was a linear negative relationship between anoxic DOC diffusion fluxes and DOC concentrations in the overlaying water (linear regression: slope: -31.3 , $R^2 = 0.55$, $p < 0.001$, data not shown). Average DOC diffusion fluxes ($3.3 \pm 5.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$) in anoxic incubations were in the same order of magnitude as anoxic and oxic sediment respiration fluxes (DIC + CH_4 : $6.83 \pm 1.14 \text{ mmol C m}^{-2} \text{ d}^{-1}$ and $10.4 \pm 6.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$, respectively) (Table 2). In the anoxic sediment incubation, CH_4 production was 18% of DIC production. In the oxic sediment incubations, a steady loss of DOC in the overlaying water was observed ($-2.9 \pm 2.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$) (Table 1).

The DOC concentration depth profile in pore water of the incubated sediments differed between anoxic and oxic treatments (Figure 5). In the sediments from anoxic incubations, profiles were relatively constant over depth and varied between 2.4 and $2.9 \text{ mmol DOC L}^{-1}$ and exceeded the concentrations in the overlaying water ($2.3 \pm 0.1 \text{ mmol DOC L}^{-1}$). In the uppermost 2 cm of sediment cores from oxic incubations, DOC pore

Table 1. Mean DOC and Fe Diffusion Fluxes From Sediments Into the Overlaying Water Under Anoxic and Oxic Conditions ($n = 4$)^a

DOC Diffusion Fluxes ($\text{mmol m}^{-2} \text{ d}^{-1}$)	Incubation Days							T_{mean}^b
	3	7	11	14	17	20	24	
Anoxic	-2.4	12	1.1	4.6	3.5	1.6	0.9	3.25
Standard deviation	2.1	4.9	3.9	3.1	1.9	0.95	0.8	5.1
Anoxic-oxic	-4.0	9.5	-8.4	14	5.6	-12	-3.1	
Standard deviation	2.6	8.8	11	16	3.2	2.8	1.8	
Oxic	-1.7	-1.4	-5.6	-3.5	-2.1	-4.2	-1.6	-2.9
Standard deviation	2.2	1.02	1.3	1.9	1.9	4.1	2.0	2.5
Fe diffusion fluxes ($\mu\text{mol m}^{-2} \text{ d}^{-1}$)	3	7	11	14	17	20	24	T_{mean}^b
Anoxic	-54	900.0	1010	240	420	220	77	434
Standard deviation	170	410	330	160	240	140	130	450
Anoxic-oxic	-86	530	550	420	780	-1300	-310	
Standard deviation	160	640	320	210	190	550	280	
Oxic	78	54	-93	80	-110	120	-110	-2.9
Standard deviation	200.0	76	10	90.0	110	110	30.0	128

^aOn day 17, the anoxic-oxic incubations were oxygenated for the remaining incubation duration. Mean values are presented in boldface.

^b T_{mean} refers to the time weighted means of individual mean rates during incubations.

Table 2. Sediment Mineralization Rates^a

	DIC (mmol m ⁻² d ⁻¹)	CO ₂ (mmol m ⁻² d ⁻¹)	CH ₄ (mmol m ⁻² d ⁻¹)	Total ^b (mmol m ⁻² d ⁻¹)	pH Change ^c
Anoxic (day 0–11)	5.91 ± 1.12	3.83 ± 0.66	0.93 ± 0.2	6.83 ± 1.14	6.9 ± 0.2–6.4 ± 0.2
Anoxic (day 11–17)	3.51 ± 0.69	2.13 ± 0.78	1.08 ± 1.16	4.59 ± 1.35	6.4 ± 0.2–6.4 ± 0.1
Anoxic T_{mean} ^d	5.1 ± 1.5	3.23 ± 1.05	0.98 ± 0.67	6.04 ± 1.61	
Oxic (day –3–0)	10.4 ± 6.7	10.3 ± 4.6	n.a.	10.4 ± 6.7	6.6 ± 0.1–6.1 ± 0.1

^aCO₂ was calculated from pH and DIC concentrations and CH₄ from GC measurements. n.a. means not analyzed.

^bSum of DIC and CH₄ fluxes.

^cpH is given for the starting and end points of the incubation periods.

^dTime weighted means of the different time points for the anoxic and oxic incubation experiments.

water concentrations were close to concentrations in the sediment overlaying oxic water ($1.4 \pm 1.5 \text{ mmol L}^{-1}$ and $1.6 \pm 0.1 \text{ mmol L}^{-1}$, respectively) and much lower than in deeper sediment layers, where pore water DOC concentrations were similar to the anoxic cores ($2.8 \pm 0.3 \text{ mmol DOC L}^{-1}$ and $2.7 \pm 0.2 \text{ mmol DOC L}^{-1}$, respectively). O₂ penetration depth at the beginning of oxic sediment incubation was calculated to $2.4 \pm 0.3 \text{ mm}$. Solid-phase sediment OC content was on average $20.4 \pm 0.6\%$ of dry weight, with minor variability between depths.

Modeling DOC concentration increase in the overlaying water using the measured sediment pore water concentrations successfully reproduced the anoxic sediment incubation results (Figure 6). Modeling of oxic sediment incubations was not attempted because no increase in DOC concentration in the water was observed, and no DOC concentration difference between pore water and water overlaying sediments was present (Figure 5). The average of measured anoxic DOC concentrations was within the error of the modeled concentration. Simulating DOC concentrations at constant water volume resulted in slightly lower (0.75–3.2%) concentrations in the overlaying water than measured during incubations. The model was most

sensitive to changes in sediment pore water concentration (C_{sed}) and diffusive boundary layer thickness. Increasing C_{sed} by 1 mmol L^{-1} (29% increase of sediment pore water concentration) resulted in a 34% increase in DOC concentration in the overlaying water at the end of incubation. Changing the diffusive boundary layer thickness from 0.16 to 0.84 mm decreased DOC concentration at the end of the experiment by 10%.

Figure 5. Depth profile of mean DOC concentrations in the pore water of the incubated sediments. Error bars indicate standard deviations ($n = 4$).

3.3. Mineralization and Flocculation in DOC Reactivity Assays

Water samples were retrieved from anoxic (A) and oxic (O) sediment incubations on day 17 and were incubated further for 40 days under anoxic (A-A, O-A) and oxic (A-O, O-O) conditions (Figure 1). Generally, the oxic water samples (A-O and O-O) showed threefold to sixfold higher CO₂ production rates compared to water incubated under anoxic conditions (A-A and O-A) (rMANOVA: $p < 0.001$) regardless of the water origin (Figure 7). In oxic water incubations, CO₂ production in water derived from anoxic sediment incubations exceeded CO₂ production in water derived from the oxic sediment incubation by ~44% (A-O > O-O, $p < 0.001$). In contrast, in the anoxic treatment CO₂ production was not significantly different between water originating from anoxic versus oxic sediment incubations

Figure 6. Comparison of DOC concentrations in the anoxic sediment incubations with modeled DOC concentrations, either with decreasing water volume at every sampling, analogous to the sediment incubation experiment (black line), or with water volume above the sediment constant (grey line). Error bars for the modeled DOC concentrations are derived from Monte Carlo simulations.

and exceeded DOC loss in the O-O incubation ($234 \mu\text{mol L}^{-1}$) by $274 \pm 87 \mu\text{mol L}^{-1}$ (~117% increase) (Figure 7). Increased CO_2 production in A-O accounted for ~23% ($63 \mu\text{mol L}^{-1}$) of this difference in DOC loss between treatments and POC formation for the remaining 77% ($211 \mu\text{mol L}^{-1}$). Total Fe concentrations at the end of incubations were similar in the treatments A-O, O-O, and O-A, ranging from 10.8 to $17.8 \mu\text{mol L}^{-1}$ (Figure 7). Only the A-A incubation exhibited with $42.8 \pm 9.5 \mu\text{mol L}^{-1}$ still elevated total Fe concentrations at the incubation end. The ratio of POC:Fe loss during A-O incubations was 10.1 ± 3.9 and total DOC:Fe loss 16.8 ± 4.7 .

3.4. DOC Optical Properties

In the anoxic sediment incubations, overlaying water increased in colored DOC (α_{420}) and aromaticity of DOC (SUVA) (Figure 8) resulting in significant differences between oxic and anoxic treatments after day 3 of sediment incubations (lme based on averages: $\alpha_{420} p < 0.001$ and SUVA $p = 0.0041$). After the anoxic sediment cores were exposed to oxygen at day 17 (anoxic-oxic treatment), colored DOC decreased to values similar to starting conditions, but SUVA values stayed elevated. A similar pattern was observed in the DOC

Figure 7. Results of DOC reactivity assays with water originating from different sediment incubations showing (a) DOC loss via flocculation (POC formation) and mineralization (CO_2 production) during the 40 days of incubation, (b) mineralization rates normalized to DOC starting concentrations during oxic and anoxic water incubations, and (c) total Fe concentrations at start and end points of the reactivity assays ($n = 4$, except for A-A, where two samples were contaminated with O_2 and, therefore, excluded from the results). A-O and O-O water samples were incubated under oxic conditions with water originating from anoxic and oxic sediment incubations, respectively. O-A and A-A water samples were incubated under anoxic conditions with water originating from oxic and anoxic sediment incubations, respectively.

Figure 8. DOM absorbance parameters from Fe(III)-corrected absorbance for color (a–c) (α_{420}) and (d–f) aromaticity (SUVA) for starting and end conditions of the sediment incubations (Figures 8a and 8d), DOC reactivity assays (Figures 8b and 8e), and field samples (Figures 8c and 8f). A-O and O-O water samples were incubated under oxic conditions with water originating from anoxic and oxic sediment incubations, respectively. O-A and A-A water samples were incubated under anoxic conditions with water originating from oxic and anoxic sediment incubations, respectively.

reactivity assays, where colored DOC in the A-O treatment (water from anoxic sediment incubated under oxic conditions) decreased to levels similar to water from oxic sediment incubations, while SUVA did not change pronouncedly. In the field survey, colored DOC in the anoxic hypolimnion showed similar and even more pronounced changes than the anoxic sediment incubation results. Values for SUVA were already elevated at the first anoxic sampling compared to the values from incubations and earlier values from the hypolimnion ($4.38 \pm 0.23 \text{ L mg}^{-1} \text{ m}^{-1}$) and stayed rather constant during anoxia.

4. Discussion

4.1. DOC Diffusion From Anoxic Sediments

This study shows that release of OC from the sediment solid phase can result in quantitatively significant DOC diffusion from the sediment of a boreal lake to the water column under anoxic conditions. In the anoxic incubations as well as in the field survey during the period of anoxic hypolimnion, DOC concentrations in the water column increased (Figures 3 and 4), which together with elevated pore water DOC concentration in anoxic sediment (Figure 5) indicates the free diffusion of pore water DOC from anoxic sediment into the water column. From marine estuarine and coastal environments there is a broad range of sediment DOC diffusion fluxes from anoxic sediment reported ($0.1\text{--}4$ and up to $50 \text{ mmol m}^{-2} \text{ d}^{-1}$ [Alkhatib et al., 2013, and references therein] and $127 \text{ mmol m}^{-2} \text{ d}^{-1}$ in marine sediment incubations by Skoog and Arias-Esquivel [2009]). While increases in DOC concentrations in anoxic lake hypolimnia have been reported previously [Brothers et al., 2014; Chadwick et al., 2006; Gonsior et al., 2013], this is the first study that assesses the relevance of the DOC diffusion flux from anoxic lake sediment by comparing it to other sediment C fluxes. Accordingly, we found that diffusion flux of DOC from sediments into anoxic lake water is an important C transport pathway from the sediment to overlaying water ($3.3 \pm 5.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$), comparable in

magnitude to C flux due to anoxic sediment mineralization ($6.8 \pm 1.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$, Table 2) and OC burial rates ($2\text{--}8.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$, from ^{210}Pb dating [Chmiel, 2015]). Other anoxic and hypoxic incubation experiments of lake sediment revealed similar DOC diffusion fluxes (2.31 ± 0.66 and $6 \text{ mmol m}^{-2} \text{ d}^{-1}$ [Dadi et al., 2015; Yang et al., 2014], respectively). To better gauge the wider importance of this process across aquatic ecosystems, we still need to better understand what influences sediment DOC diffusion fluxes.

4.2. Potential Processes Involved in Anoxic DOC Diffusion

With the chosen incubation setup, the derived fluxes were affected by decreasing volume from repeated sampling. The model we used to quantify this effect reproduced well the measured concentrations in the incubations (Figure 6). DOC diffusion fluxes assuming a constant water volume were only slightly slower than observed DOC diffusion, leading to marginally lower DOC concentrations in the overlaying water at the end of the experiment compared to measured DOC concentrations. Since it was possible to model concentration increase in the water column assuming constant pore water concentration (i.e., without accounting for any potential decrease of pore water DOC concentration as a result of DOC diffusing out from the sediment), this suggests that the rate of DOC release from sediment into pore water takes place at a rate not smaller than DOC diffusion across the sediment water interface. Accordingly, in the anoxic sediment pore water, no depletion in DOC pore water concentration could be observed in topmost sediment layers (Figure 5), even if this observation may be confined by the relatively coarse depth resolution at sampling (1 cm).

Sediments incubated under anoxic conditions exhibited a homogeneously high DOC pore water concentration over sediment depth, while in oxic incubations, DOC pore water concentration decreased toward the sediment water interface (Figure 5). The different pore water DOC concentrations in the anoxic and oxic sediments might be explained by the reduction of Fe(III) to Fe(II) and the concomitant dissolution of DOC into pore water under anoxic conditions and by trapping of DOC in oxic sediment layers through resorption to Fe(III), thereby preventing its diffusion out into the water column [O'loughlin and Chin, 2004; Skoog and Arias-Esquivel, 2009]. Accordingly, only in the anoxic sediment incubations and anoxic lake hypolimnion, DOC increase in the overlaying water was observed (Figures 3 and 4). In oxic incubations, DOC concentrations in the overlaying water even decreased during the incubation, probably due to respiration (some biofilm formation was observed on the walls of the incubation tubes) and flocculation. The simultaneous increase in Fe(II) and DOC concentrations in the anoxic sediment incubations as well as in the anoxic lake hypolimnion indicates a close coupling of reductive dissolution of Fe and DOC, similar to the effect of iron redox cycling on the release of, e.g., phosphorus and arsenic from anoxic lake sediments [Li et al., 2012; Smedley and Kinniburgh, 2013]. DOC concentrations in pore water from both marine and freshwater sediments can vary greatly from 0.4 up to 27 mmol L^{-1} [e.g., Alkhatib et al., 2013; Mozeto et al., 2001; O'loughlin and Chin, 2004; Wang et al., 2013; Yang et al., 2014], and it is unclear how large the contribution of DOC release through reductive Fe dissolution is. Both Fe and OC might additionally bind to other substances (e.g., to manganese or phosphate) and undergo additional preservation and release processes. There is indication that binding to OC can protect a large part of Fe from reduction [Lalonde et al., 2012] and that iron-OC coprecipitates can vary strongly in their dissolution behavior compared to pure Fe oxides [Kieber et al., 2015]. Also, other redox-sensitive compounds like manganese and sulfides might play a role in DOC and iron mobility in sediments [Skoog and Arias-Esquivel, 2009; Tessier et al., 1996]. Furthermore, high dissimilatory reduction activity can lead to pH increase through proton consumption and weaken the overall binding of DOC to the particulate phase, thereby rendering it more soluble [Grybos et al., 2009]; and microbial hydrolytic activity can additionally contribute to DOC release from POC. However, pH in the water overlaying sediments dropped from 6.9 to 6.4 during anoxic sediment incubation due to respiratory CO_2 production (Table 2). Hence, pH change was probably not responsible for increased leaching of DOC into pore water. Furthermore, there might be a saturation concentration for both Fe(II) and DOC that can be dissolved into pore water, as the rather constant pore water concentrations in the anoxic sediment cores suggest (Figure 5). However, even if the detailed processes behind DOC release into the pore water of anoxic sediment remain incompletely understood, our data in concert with the published literature make it highly plausible that dissolution of OC from Fe(III) after reduction to Fe(II) is the main pathway to release DOC into pore water of the studied boreal lake sediment. In particular, the synchronicity of DOC and Fe(II) concentration increase in anoxic sediment incubations as well as in the anoxic lake hypolimnion (Figures 3 and 4) strongly supports this conclusion.

The molar ratio of DOC to Fe that was released until the end of the incubation ($\Delta\text{DOC}:\Delta\text{Fe} = 7.7 \pm 0.7$) and that accumulated in the anoxic lake hypolimnion ($\Delta\text{DOC}:\Delta\text{Fe} = 6.7 \pm 1.3$) corresponds well with the published molar ratios of OC bound to Fe found in soils (6–10 [Wagai and Mayer, 2007]) and was slightly higher than the observed ratios for continental margin sediments (4 ± 2.8 [Lalonde et al., 2012]) and ratios for DOC to Fe diffusing from marine sediments (4.6 [Skoog and Arias-Esquivel, 2009]). Furthermore, SUVA and absorbance values point toward characteristics of the released OC (terrestrial high molecular weight and aromatic organic carbon) that are typical for OC that preferentially sorbs to Fe (Figure 8) [Chin et al., 1998; Mladenov et al., 2009; Riedel et al., 2013]. It seems also very reasonable that the restricted DOC diffusion under oxic conditions is related to the sorption of DOC to Fe(III) in the upper oxic sediment layers, highlighting the importance of OC-Fe interactions under different redox conditions.

The delayed start of iron and DOC diffusion (>3 days after anoxia was induced) in the sediment incubation experiment may be explained by traces of O_2 still present and more energy yielding processes (e.g., nitrate reduction) taking place prior Fe(III) reduction. In marine sediment incubations, similar increases in DOC and Fe concentrations were observed [Skoog and Arias-Esquivel, 2009]. The absolute DOC concentration increase is in the same order of magnitude for both studies. However, in the marine study by Skoog and Arias-Esquivel [2009], DOC and Fe concentrations increased more rapidly and dropped after 4 days of incubation. This was explained by the formation of iron sulfides causing Fe and DOC precipitation. It seems plausible that in freshwater, where sulfur concentrations are orders of magnitude smaller than in marine water [Holmer and Storkholm, 2001], precipitation of Fe(II) with sulfides should be less prevalent. Hence, in freshwater systems the length of the anoxic period will greatly define how much DOC is diffusing into the overlying water, whereas in marine systems, diffusion might cease earlier due to reactions with sulfides.

4.3. Lake Hypolimnetic DOC Increase

DOC and iron concentrations increased similarly in situ as in the sediment incubation experiments, suggesting that sediment DOC diffusion was the main contribution to raising DOC concentrations also in the lake hypolimnion. Precipitation events toward the end of the stable stratification period (10–14 and 17–22 August) (Figures 2 and 3) resulted in DOC input from the catchment to the epilimnion, but any potential entrainment of epilimnetic water into the hypolimnion was not apparent from the continuous temperature, conductivity, and dissolved oxygen data (Figure 2). The Schmidt stability of the water column was high during the period of hypolimnetic anoxia (Figure S3), indicating that no mixing of epilimnetic water with hypolimnetic water occurred between 10 May and 19 August. Similarly, the stable specific conductivity values in the hypolimnion during the anoxic period (Figure 2) and the strong linear relationship between hypolimnetic DOC and specific conductivity ($R^2 = 0.94$, $p < 0.001$, Fig. S4) further support the existence of an undisturbed hypolimnion and exclude a possible inflow from high DOC and low-conductivity epilimnetic water as a source for hypolimnetic DOC (Figure 3). However, diffusion of DOC from the epilimnion to the hypolimnion or release of DOC from sedimenting organic particles may have contributed to the observed hypolimnetic DOC increase during anoxia. Calculated diffusion flux from the DOC-rich epilimnion over the oxycline to the hypolimnion was, however, too low (0.005 and $0.02 \text{ mmol m}^{-2} \text{ d}^{-1}$ for 0.5 and 0.1 m diffusion layer thickness, respectively) to sustain the observed increase in hypolimnetic DOC concentration ($4.7 \pm 0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$). Similarly, the residence time of sinking and potentially dissolving organic-rich particles in this very shallow hypolimnion is very short ($\sim 2 \text{ h}$) [Boudreau and Jorgensen, 2001], and the quantity of sinking POC at any point of time is negligible compared to standing stock of POC in surficial sediment [von Wachenfeldt and Tranvik, 2008]. Hence, it is unlikely that dissolution of POC during sinking and before reaching the lake bottom provides a significant source for DOC to the hypolimnion. Moreover, whether POC dissolution takes place in the anoxic water column or on the lake bottom is irrelevant to the conclusion that OC release from POC is driving the observed hypolimnetic DOC increase. Lastly, bioturbation may be relevant for in situ sediment fluxes. Although bioturbation under anoxic conditions is generally strongly reduced, previous worm burrows could additionally aid the diffusion of anaerobic compounds out of the sediments into the water column [Sturdivant et al., 2012].

4.4. Fate and Characteristics of DOC Diffusing From Anoxic Sediments

The presence or absence of oxygen had the strongest impact on DOC loss in the DOC reactivity assays, regardless of the DOC origin, i.e., water that was incubated under oxic conditions (O-O and A-O) showed higher DOC losses than anoxic water (O-A and A-A; Figure 7). Anoxic water incubations also revealed no

difference in DOC loss between water originating from anoxic (A-A) and oxic (O-A) sediment incubations, indicating no effect of anoxic DOC diffusion on DOC mineralization and flocculation rates in anoxic water. In contrast, oxic or anoxic origin of the water resulted in differences in DOC loss when incubated at oxic conditions. At oxic conditions, DOC originating from anoxic sediment incubations (A-O) showed higher DOC loss than oxic water (O-O; Figure 7). Similarly, in the anoxic-oxic sediment incubations it was observed that DOC removal rate after reoxygenation of the water was faster than in oxic incubations (12 ± 2.8 and 3.1 ± 1.8 versus $2.9 \pm 2.5 \text{ mmol m}^{-2} \text{ d}^{-1}$), with the highest rates in the first 3 days (Figure 4 and Table 1). After 7 days of oxygenation, DOC concentrations in the anoxic-oxic sediment incubations were similar to starting concentrations. This indicates that after mixing of the lake, DOC originating from the sediment will be rapidly lost from the water column. In the field survey, DOC loss at mixing could unfortunately not be observed because of a pronounced increase in surface water DOC toward the end of stratification, triggered by a major precipitation event.

The ratio of DOC:Fe loss during the oxidation of anoxic sediment incubations (anoxic-oxic) (9.6 ± 2.2) and in the A-O DOC reactivity assay (16.8 ± 4.7) was higher than the ratios of DOC:Fe diffusion in the sediment incubations. This corroborates the observation in the DOC reactivity assays that after oxygenation of previously anoxic water, POC formation through sorption to Fe(III) was the dominant DOC removal process (~77% of diffused DOC), but that CO_2 production additionally contributed to the DOC loss (~23% of diffused DOC; Figure 7). Similarly, *Satoh et al.* [2006] identified DOC sorption to Fe(III) as the main mechanism for DOC loss during oxygenation of anoxic lake hypolimnion water. We calculated POC formation rates in the oxic-anoxic sediment incubations of $9.2 \pm 2.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ (day 20) and $2.4 \pm 1.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ (day 24) (77% of DOC flux during that incubation time), which are higher than values reported from other boreal systems ($1.25 \text{ mmol m}^{-2} \text{ d}^{-1}$) by *von Wachenfeldt et al.* [2008]. This may indicate that the diffusing DOC and the reoxidized Fe(III) have a strong affinity for resorption and subsequent flocculation and sedimentation. Hence, transitions periods from anoxic to oxic periods likely lead to increased sedimentation of POC in the water column of boreal lakes.

However, part of the diffusing DOC from anoxic sediment can also be mineralized when oxic conditions are reestablished. We calculated the portion of the flux of DOC from anoxic sediments that will be mineralized to be $0.74 \text{ mmol m}^{-2} \text{ d}^{-1}$ (23% of the anoxic DOC diffusion). This part of the diffusing DOC constitutes a permanent loss of carbon from the sediment and increases overall OC mineralization in anoxic sediments ($5.1 \text{ mmol m}^{-2} \text{ d}^{-1}$) by ~15%. This is likely a conservative estimate of OC loss through this pathway, because DOC mineralization was measured as CO_2 production in the DOC reactivity assays, and not as DIC production, which would have rendered about 34% higher mineralization rates in the A-O incubation (Figure S1). Consequently, also the percentage of OC loss through POC formation might be overestimated with our approach, since total DOC loss is underestimated when based on CO_2 instead of DIC production. Furthermore, the results from the DOC reactivity assays represent a snapshot in the process of diffusing DOC, and ecosystem-scale generalizations from these results should be taken with care.

The observed increased CO_2 production rates in oxic water incubation originating from anoxic sediment incubation (A-O) disappeared when CO_2 production was normalized to DOC concentration. This indicates that increased mineralization in A-O treatment resulted from the magnitude of DOC release from anoxic sediment, and not from elevated reactivity of the DOC release from anoxic sediment ($\text{A-O} \approx \text{O-O}$ and $\text{A-A} > \text{O-A}$) (Figure 7). We need to consider, however, that the results from the DOC reactivity assay do not account for potential changes in DOC quality during the incubation, both in the oxic and anoxic sediment incubations. For example, our experimental setup cannot resolve the potential effect of highly bioavailable low molecular weight organic compounds because they can be consumed very rapidly even under anoxic conditions. While water color increased significantly during anoxia, it also rapidly decreased to preanoxic levels after oxygenation of the water (Figure 8), indicating that DOC diffusion from anoxic sediments is not contributing to increased water color in oxic surface waters [*Kritzberg and Ekström*, 2012; *Weyhenmeyer et al.*, 2014]. On the other hand, DOC diffusion seemed to have an effect on the composition of the DOC pool in the reoxygenated water by increasing the contribution of aromatic organic carbon compounds, as indicated by the still slightly elevated SUVA values after reoxygenation of water in the sediment incubations and the DOC reactivity assay (Figure 8). This was a surprising result, since commonly SUVA and water color are closely related and we cannot exclude a potential artifact caused by the correction for iron absorbance. In uncorrected SUVA results,

the discrepancy between anoxic and anoxic-oxic water and A-O and A-A samples was more pronounced due to Fe(III) absorbance (Figure S5). Generally, absorbance measurements of anoxic water samples need to be interpreted carefully because of the different absorbance characteristics of Fe(II) and Fe(III) [Poulin *et al.*, 2014]. It is difficult to ensure anoxic conditions during measurements in order to keep all Fe as Fe(II) and hence not exhibiting an effect on absorbance. But on the other hand, oxidizing the sample prior to measurements in order to guarantee that all iron is present as Fe(III) might also induce unwanted alterations in the DOM pool (e.g., flocculation). The iron correction for absorbance measurements may also not account for specific absorbance resulting from iron-DOM interactions (e.g., charge transfer), potentially explaining the observed offset between SUVA and water color.

4.5. Implications for Lake C Dynamics

Even though anoxic sediments are known as sites of efficient OC burial [Gélinas *et al.*, 2001; Sobek *et al.*, 2009], our study shows that considerable amounts of OC can be released from the solid phase and diffuse from anoxic sediments into the water, at rates in the same order of magnitude as OC is buried [Chmiel, 2015] and mineralized in sediments. We estimate that DOC diffusion from the studied boreal lake sediment and subsequent mineralization in oxic water can increase the OC loss from anoxic sediments (~15%), as a proportion of the DOC that has been released from anoxic sediment is mineralized in the water column. Comparing to the overall lake carbon budget, however, DOC diffusion is rather negligible. For example, Chmiel [2015] found that anoxic sediment mineralization in Lake Erssjön, which is of similar magnitude as sediment DOC diffusion, accounted for only 3% of whole lake OC mineralization. Similarly, the mineralization of DOC originating from anoxic sediment ($0.74 \text{ mmol m}^{-2} \text{ d}^{-1}$) is a negligible contribution to lake CO_2 emissions (daily median CO_2 flux from the lake to the atmosphere: $39.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ [Chmiel, 2015]).

Considering the sediment carbon budget instead, DOC diffusion from anoxic sediments may have implications when the sediment OC burial efficiency (OC burial/OC deposition) is calculated, since OC deposition is often calculated by summing OC burial and sediment mineralization (i.e., OC deposition = OC burial + OC mineralization). In Lake Erssjön, OC burial, based on sediment core ^{210}Pb dating, at the deepest point of the lake ranged between 1.9 and 8.4 (mean 3.8) $\text{mmol m}^{-2} \text{ d}^{-1}$ [Chmiel, 2015]. The OC burial efficiency calculated with the mean burial rate and sediment mineralization (Table 2) was considerably lower if calculated for oxic (27%) than for anoxic sediments (38%), due to the difference in mineralization rates. However, adding the previously unaccounted DOC loss via diffusion from anoxic sediment (i.e., OC deposition = OC burial + OC mineralization + DOC diffusion) lowers the OC burial efficiency in anoxic sediments from 38% to 29%. But since we estimated that only ~23% of the DOC that was lost from the sediment was mineralized, and ~77% flocculated and again formed sediment after exposure to oxygen, this number would be misleading. Accordingly, we calculated an OC burial efficiency of anoxic sediments of 36% when accounting only for permanent C loss from anoxic sediment via water column mineralization of DOC originating from anoxic sediment. These calculations show that in order to gauge the effect of DOC loss from anoxic sediment on the OC burial efficiency, it is a key to determine the fraction of the sediment-derived DOC that is permanently lost via mineralization, and this fraction may be different for different lakes or sediments.

It should further be noted that DOC diffusion from anoxic sediment can also affect the OC burial efficiency if calculated using sediment traps to derive OC deposition flux onto the sediment: since traps are likely to catch sediment-derived DOC that precipitates upon reoxygenation and again settles to the sediment, an overestimation of OC deposition is probable and leads to an underestimation of the OC burial efficiency. Possibly, this effect can be sizeable if, as in Lake Erssjön, the majority of the DOC originating from the sediment flocculated upon oxygenation.

Lake Erssjön is an organic-rich boreal lake with high terrestrial DOC concentration in the water and high sediment OC content and represents an end-member in that respect. von Wachenfeldt and Tranvik [2008] showed that terrestrial DOC is an important precursor for sediment in boreal lakes and that iron, next to light and temperature, is involved in the process of DOC flocculation and sedimentation. Similarly, Riedel *et al.* [2013] highlighted the importance of terrestrial DOC and iron for the formation of POC. The high contribution of terrestrial DOC in Lake Erssjön might have increased the susceptibility of the lake for OC-Fe interactions, and the contribution of DOC settling with Fe is likely to be high. The observed concomitant increase of DOC and Fe(II) concentration in anoxic water (Figures 3 and 4) points toward a specific release of

Fe-associated OC, potentially rendering humic boreal lakes like Lake Erssjön extreme cases for DOC diffusion from anoxic sediment. Therefore, it remains to be further investigated how far the results of this study could be applicable to other lakes. It is likely that pH affects the association of DOC with iron [Jansen *et al.*, 2002], i.e., at higher pH more DOC is expected to be released into sediment pore water. The availability of nutrients can limit microbial activity and hence might be important in determining the rate of iron reduction in sediments, i.e., in oligotrophic lakes the release of DOC during iron reduction might be a rate-limiting step for DOC diffusion from sediments into the water column. In saline lakes or marine systems, sulfides play an important role by capturing Fe(II) in the sediment, limiting the amount of iron available for oxidation and sorption of DOC. Also, salinity was reported to influence the solubility of iron in the water mainly through enhancing coprecipitation of Fe together with organic material [Kritzberg *et al.*, 2014]. However, since DOC diffusion from anoxic sediments was also reported from a marine system, very low in DOC and nutrients [Skoog and Arias-Esquivel, 2009], we suspect that DOC diffusion from anoxic sediment can be relevant over a wide range of environmental conditions, even if it is likely that rates will differ between different aquatic systems.

Stratification is expected to become stronger and longer lasting with climate change, such that hypolimnetic anoxia is likely to become more prevalent in the future [Jankowski *et al.*, 2006]. This process may be particularly pronounced in lakes experiencing increases in humic content, since the humic matter absorbs light and heat, implying a stronger heating of surficial layers, and thereby more rapid and stable stratification [Brothers *et al.*, 2014; von Einem and Granéli, 2010]. Also, eutrophic lakes are more prone to develop anoxic hypolimnia due to high sediment mineralization rates [Gudasz *et al.*, 2010] and hence more likely to release DOC from their sediments in response to stronger stratification. The importance of redox-mediated processes, like the release of DOC during iron reduction, may therefore increase in the future, potentially increasing carbon loss from anoxic sediment by DOC diffusion.

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References

- Alkhatib, M., P. del Giorgio, Y. Gelinas, and M. Lehmann (2013), Benthic fluxes of dissolved organic nitrogen in the lower St. Lawrence estuary and implications for selective organic matter degradation, *Biogeosciences*, 10(11), 7609–7622.
- Berner, R., P. Uni, and D. L. Graf (1980), *Early Diagenesis: Theoretical Approach*, 241 pp., Princeton, N. J.
- Boudot, J. (1989), Biodegradation of synthetic organo-metallic complexes of iron and aluminium with selected metal to carbon ratios, *Soil Biol. Biochem.*, 21(7), 961–966.
- Boudreau, B. P. (1997), *Diagenetic Models and Their Implementation: Modelling Transport and Reactions in Aquatic Sediments*, Springer, Heidelberg.
- Boudreau, B. P., and B. B. Jorgensen (2001), *The Benthic Boundary Layer: Transport Processes and Biogeochemistry*, Oxford Univ. Press, New York.
- Brand, A., C. Dinkel, and B. Wehrli (2009), Influence of the diffusive boundary layer on solute dynamics in the sediments of a seiche-driven lake: A model study, *J. Geophys. Res.*, 114, G01010, doi:10.1029/2008JG000755.
- Broman, E. (2013), *Observation of Methanogenesis and Potential Iron-Dependent Anaerobic Oxidation of Methane in Old Lake Sediments, A study of Two Boreal Forest Lakes*, Uppsala Univ., Uppsala, Sweden.
- Brothers, S., J. Köhler, K. Attermeyer, H. Grossart, T. Mehner, N. Meyer, K. Scharnweber, and S. Hilt (2014), A feedback loop links brownification and anoxia in a temperate, shallow lake, *Limnol. Oceanogr.*, 59(4), 1388–1398.
- 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.
- Chadwick, S. P., C. L. Babiarez, J. P. Hurley, and D. E. Armstrong (2006), Influences of iron, manganese, and dissolved organic carbon on the hypolimnetic cycling of amended mercury, *Sci. Total Environ.*, 368(1), 177–188.
- 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, *Limnol. Oceanogr.*, 43(6), 1287–1296.
- Chmiel, H. E. (2015), *The role of sediments in the carbon cycle of boreal lakes*, PhD dissertation, Uppsala Univ., Uppsala, Sweden.
- Cole, J. J., et al. (2007), Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, *Ecosystems*, 10(1), 171–184, doi:10.1007/s10021-006-9013-8.
- Crawley, M. J. (Ed.) (2007), Mixed-effects models, in *The R Book*, 2nd ed., pp. 681–714, John Wiley, West Sussex, England.
- 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*, 15, 2350–2358.
- Fee, E., R. Hecky, S. Kasian, and D. Cruikshank (1996), Effects of lake size, water clarity, and climatic variability on mixing depths in Canadian Shield lakes, *Limnol. Oceanogr.*, 41(5), 912–920.
- Gélinas, Y., J. A. Baldock, and J. I. Hedges (2001), Organic carbon composition of marine sediments: Effect of oxygen exposure on oil generation potential, *Science*, 294(5540), 145–148.
- Gonsior, M., P. Schmitt-Kopplin, and D. Bastviken (2013), Depth-dependent molecular composition and photo-reactivity of dissolved organic matter in a boreal lake under winter and summer conditions, *Biogeosciences*, 10(11), 6945–6956.
- Grybos, M., M. Davranche, G. Gruau, P. Petitjean, and M. Pédrot (2009), Increasing pH drives organic matter solubilization from wetland soils under reducing conditions, *Geoderma*, 154(1), 13–19.
- 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(7305), 478–481.
- Gudasz, C., S. Sobek, D. Bastviken, B. Koehler, and L. J. Tranvik (2015), Temperature sensitivity of organic carbon mineralization in contrasting lake sediments, *J. Geophys. Res. Biogeosci.*, 120, 1215–1225, doi:10.1002/2015JG002928.
- Gueorguieva, R., and J. H. Krystal (2004), Move over ANOVA: Progress in analyzing repeated-measures data and its reflection in papers published in the archives of general psychiatry, *Arch. Gen. Psychiatry*, 61(3), 310–317.

- Hartnett, H. E., R. G. Keil, J. I. Hedges, and A. H. Devol (1998), Influence of oxygen exposure time on organic carbon preservation in continental margin sediments, *Nature*, *391*, 572–574.
- Hedges, J. I., F. S. Hu, A. H. Devol, H. E. Hartnett, E. Tsamakis, and R. G. Keil (1999), Sedimentary organic matter preservation: A test for selective degradation under oxic conditions, *Am. J. Sci.*, *299*(7–9), 529–555.
- Holmer, M., and P. Storkholm (2001), Sulphate reduction and sulphur cycling in lake sediments: A review, *Freshwater Biol.*, *46*(4), 431–451.
- Hothorn, T., F. Bretz, and P. Westfall (2008), Simultaneous inference in general parametric models, *Biom. J.*, *50*(3), 346–363.
- Hu, C., F. E. Muller-Karger, and R. G. Zepp (2002), Absorbance, absorption coefficient, and apparent quantum yield: A comment on common ambiguity in the use of these optical concepts, *Limnol. Oceanogr.*, *47*(4), 1261–1267.
- Jankowski, T., D. M. Livingstone, H. Bührer, R. Forster, and P. Niederhauser (2006), Consequences of the 2003 European heat wave for lake temperature profiles, thermal stability, and hypolimnetic oxygen depletion: Implications for a warmer world, *Limnol. Oceanogr.*, *51*(2), 815–819, doi:10.4319/lo.2006.51.2.0815.
- Jansen, B., K. G. Nierop, and J. M. Verstraten (2002), Influence of pH and metal/carbon ratios on soluble organic complexation of Fe (II), Fe (III) and Al (III) in soil solutions determined by diffusive gradients in thin films, *Anal. Chim. Acta*, *454*(2), 259–270.
- Jones, D., and A. Edwards (1998), Influence of sorption on the biological utilization of two simple carbon substrates, *Soil Biol. Biochem.*, *30*(14), 1895–1902.
- 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*(7), 711–725.
- 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*(6490), 549–552.
- Kleber, M., K. Eusterhues, M. Keiluweit, C. Mikutta, R. Mikutta, and P. S. Nico (2015), Mineral–organic associations: Formation, properties, and relevance in soil environments, *Adv. Agron.*, *130*, 1–140, doi:10.1016/bs.agron.2014.10.005.
- Klemetsson, L. (2012), *The Skogaryd Research Site-Integration of Terrestrial and Freshwater Greenhouse Gas Sources and Sinks*, 7454 pp., EGU, Vienna.
- 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*(2), 891–904.
- Köhler, S. J., D. Kothawala, M. N. Futter, O. Liungman, and L. Tranvik (2013), In-lake processes offset increased terrestrial inputs of dissolved organic carbon and color to lakes, *Plos One*, *8*(8), e70598, doi:10.1371/journal.pone.0070598.
- Kritzberg, E., and S. Ekström (2012), Increasing iron concentrations in surface waters—A factor behind brownification?, *Biogeosciences*, *9*, 1465–1478.
- Kritzberg, E. S., A. B. Villanueva, M. Jung, and H. E. Reader (2014), Importance of boreal rivers in providing iron to marine waters, *Plos One*, *9*(9), e107500.
- Lalonde, K., A. Mucci, A. Ouellet, and Y. Gélinais (2012), Preservation of organic matter in sediments promoted by iron, *Nature*, *483*(7388), 198–200.
- Li, Y., S. Yu, J. Strong, and H. Wang (2012), Are the biogeochemical cycles of carbon, nitrogen, sulfur, and phosphorus driven by the “FeIII–FeII redox wheel” in dynamic redox environments?, *J. Soils Sediments*, *12*(5), 683–693.
- Mladenov, N., Y. Zheng, M. P. Miller, D. R. Nernberg, T. Legg, B. Simone, C. Hageman, M. M. Rahman, K. M. Ahmed, and D. M. McKnight (2009), Dissolved organic matter sources and consequences for iron and arsenic mobilization in Bangladesh aquifers, *Environ. Sci. Technol.*, *44*(1), 123–128, doi:10.1021/es901472g.
- Mozeto, A. A., P. C. F. Silvério, and A. Soares (2001), Estimates of benthic fluxes of nutrients across the sediment–water interface (Guarapiranga reservoir, São Paulo, Brazil), *Sci. Total Environ.*, *266*(1), 135–142.
- O’loughlin, E. J., and Y. P. Chin (2004), Quantification and characterization of dissolved organic carbon and iron in sedimentary porewater from Green Bay, WI, USA, *Biogeochemistry*, *71*(3), 371–386.
- Poulin, B. A., J. N. Ryan, and G. R. Aiken (2014), Effects of iron on optical properties of dissolved organic matter, *Environ. Sci. Technol.*, *48*(17), 10,098–10,106, doi:10.1021/Es502670r.
- Riedel, T., D. Zak, H. Biester, and T. Dittmar (2013), Iron traps terrestrially derived dissolved organic matter at redox interfaces, *Proc. Natl. Acad. Sci. U.S.A.*, *110*(25), 10,101–10,105.
- Rydin, H., P. Snoeijis, and M. Diekmann (Eds) (1999), *Swedish Plant Geography*, Svenska Vaxtgeografiska Sällskapet, Uppsala, Sweden.
- Satoh, Y., K. Kikuchi, S. Kinoshita, and H. Sasaki (2006), Potential capacity of coprecipitation of dissolved organic carbon (DOC) with iron(III) precipitates, *Limnology*, *7*, 231–235, doi:10.1007/s10201-006-0184-y.
- 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*(23), 6085–6092.
- Skoog, A., P. O. J. Hall, S. Hulth, N. Paxéus, M. R. Van Der Loeff, and S. Westerlund (1996), Early diagenetic production and sediment–water exchange of fluorescent dissolved organic matter in the coastal environment, *Geochim. Cosmochim. Acta*, *60*(19), 3619–3629.
- Smedley, P., and D. G. Kinniburgh (2013), *Arsenic in Groundwater and the Environment*, Springer, New York.
- Sobek, S., L. J. Tranvik, Y. T. Prairie, P. Kortelainen, and J. J. Cole (2007), Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes, *Limnol. Oceanogr.*, *52*(3), 1208–1219.
- Sobek, S., E. Durisch-Kaiser, R. Zurbrugg, N. Wongfun, M. Wessels, N. Pasche, and B. Wehrli (2009), Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source, *Limnol. Oceanogr.*, *54*(6), 2243–2254.
- Sobek, S., J. Nisell, and J. Fölster (2011), Predicting the volume and depth of lakes from map-derived parameters, *Inland Waters*, *1*(3), 177–184.
- Sturdivant, S. K., R. J. Diaz, and G. R. Cutter (2012), Bioturbation in a declining oxygen environment, in situ observations from wormcam, *Plos One*, *7*(4), e34539.
- Tessier, A., D. Fortin, N. Belzile, R. DeVitre, and G. Leppard (1996), Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: Narrowing the gap between field and laboratory measurements, *Geochim. Cosmochim. Acta*, *60*(3), 387–404.
- Thurman, E. (1985), *Organic Geochemistry of Natural Waters*, Martinus Nijhoff, Dordrecht, Netherlands.
- Tipping, E., and C. Woof (1983), Seasonal variations in the concentrations of humic substances in a soft-water lake, *Limnol. Oceanogr.*, *28*(1), 168–172, doi:10.4319/lo.1983.28.1.0168.
- Verschoor, M. J., and L. A. Molot (2013), A comparison of three colorimetric methods of ferrous and total reactive iron measurement in freshwaters, *Limnol. Oceanogr. Methods*, *11*(3), 113–125.
- Viollier, E., P. Inglett, K. Hunter, A. Roychoudhury, and P. Van Cappellen (2000), The ferrozine method revisited: Fe (II)/Fe (III) determination in natural waters, *Appl. Geochem.*, *15*(6), 785–790.
- von Einem, J., and W. Granéli (2010), Effects of fetch and dissolved organic carbon on epilimnion depth and light climate in small forest lakes in southern Sweden, *Limnol. Oceanogr.*, *55*(2), 920–930.

- 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(5), 803–814.
- von Wachenfeldt, E., S. Sobek, D. Bastviken, and L. J. Tranvik (2008), Linking allochthonous dissolved organic matter and boreal lake sediment carbon sequestration: The role of light-mediated flocculation, *Limnol. Oceanogr.*, 53, 2416–2426.
- Wagai, R., and L. M. Mayer (2007), Sorptive stabilization of organic matter in soils by hydrous iron oxides, *Geochim. Cosmochim. Acta*, 71(1), 25–35.
- Wang, Y., D. Zhang, Z. Shen, C. Feng, and J. Chen (2013), Revealing sources and distribution changes of dissolved organic matter (DOM) in pore water of sediment from the Yangtze estuary, *Plos One*, 8(10), e76633.
- 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, *Environ. Sci. Technol.*, 37(20), 4702–4708.
- Weiss, R. F. (1974), Carbon dioxide in water and seawater: The solubility of a non-ideal gas, *Mar. Chem.*, 2(3), 203–215.
- Weyhenmeyer, G. A., Y. T. Prairie, and L. J. Tranvik (2014), Browning of boreal freshwaters coupled to carbon-iron interactions along the aquatic continuum, *Plos One*, 9(2), e88104.
- Yamamoto, S., J. B. Alcauskas, and T. E. Crozier (1976), Solubility of methane in distilled water and seawater, *J. Chem. Eng. Data*, 21(1), 78–80.
- 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.