

Particles and Aeration at Mire-Stream Interfaces Cause Selective Removal and Modification of Dissolved Organic Matter

Karólína Einarsdóttir¹ , Katrin Attermeyer^{1,2} , Jeffrey A. Hawkes³ , Dolly Kothawala¹ , Ryan A. Sponseller⁴ , and Lars J. Tranvik¹ 

¹Limnology, Department of Ecology and Genetics, Uppsala University, Uppsala, Sweden, ²Now at Wasser Cluster Lunz, Lunz am See, Austria, ³Department of Chemistry, BMC, Uppsala University, Uppsala, Sweden, ⁴Department of Ecology and Environmental Sciences, Umeå University, Umeå, Sweden

Key Points:

- After aeration, hydrophilic and amphiphilic, nitrogen-poor aromatic species coprecipitated with oxidized iron
- Peat-derived particles promoted retention of nitrogen species and nonaromatic DOM, and stimulated microbial activity
- Half of the oxygen removal was attributed to nonrespiratory oxygen consumption

Supporting Information:

- Supporting Information S1

Correspondence to:

K. Einarsdóttir,
karolina.einarsdottir@ebc.uu.se

Citation:

Einarsdóttir, K., Attermeyer, K., Hawkes, J. A., Kothawala, D., Sponseller, R. A., & Tranvik, L. J. (2020). Particles and aeration at mire-stream interfaces cause selective removal and modification of dissolved organic matter. *Journal of Geophysical Research: Biogeosciences*, 125, e2020JG005654. <https://doi.org/10.1029/2020JG005654>

Received 17 JAN 2020

Accepted 6 OCT 2020

Accepted article online 11 NOV 2020

Author Contributions:

Conceptualization: Karólína Einarsdóttir

Data curation: Karólína Einarsdóttir, Jeffrey A. Hawkes

Formal analysis: Karólína Einarsdóttir, Katrin Attermeyer, Jeffrey A. Hawkes

Funding acquisition: Karólína Einarsdóttir, Katrin Attermeyer, Lars J. Tranvik

Investigation: Karólína Einarsdóttir, Katrin Attermeyer

Methodology: Karólína Einarsdóttir, Katrin Attermeyer, Jeffrey A. Hawkes
(continued)

Abstract Peatlands are dominant sources of dissolved organic matter (DOM) to boreal inland waters and play important roles in the aquatic carbon cycle. Yet before peat-derived DOM enters aquatic networks, it needs to pass through peat-stream interfaces that are often characterized by transitions from anoxic or hypoxic to oxic conditions. Aeration at these interfaces may trigger processes that impact the DOM pool, and its fate downstream. Here we experimentally assessed how the aeration of iron- and organic-rich mire-waters influences biodegradation, particle-formation, and modification of DOM. In addition, we investigated how suspended peat-derived particles from mires may influence these processes. We found that within 5 days of aeration, 20% of the DOM transformed into particulate organic matter (POM). This removal was likely due to combination of mechanisms including coprecipitation with oxidized iron, aggregation, and DOM-adsorption onto peat-derived particles. Peat-derived particles promoted microbial activity, but biodegradation was a minor loss mechanism of DOM removal. Interestingly, microbial respiration accounted for only half of the oxygen loss, suggesting substantial nonrespiratory oxygen consumption. The differences observed in DOM characteristics between anoxic and aerated treatments suggest that hydrophilic, aromatic DOM coprecipitated with iron oxides in aerated samples, and the corresponding C:N analysis of generated POM revealed that these organic species were nitrogen-poor. Meanwhile, POM formed via adsorption onto peat-derived particles generated from nonaromatic DOM and more nitrogen-rich species. Hence, selective removal of DOM, dissolved iron, and thus oxygen may be important and overlooked processes in mire-dominated headwater systems.

Plain Language Summary Substantial amounts of dissolved organic matter are discharged from boreal peatlands into small streams and delivered to downstream rivers and lakes, impacting water quality, freshwater ecology, and the aquatic carbon cycle. About half of this dissolved organic matter is processed and removed during downstream transport, mainly via degradation and CO₂ emission, but also through particle formation and sedimentation. Less is known about the processing in upstream systems, where peat-water emerges into small streams. These peat-stream interfaces are characterized by rapid transitions from anoxic to oxic conditions. Since oxygen exposure may promote both microbial activity and chemical reactions, e.g., coprecipitation with iron, these interfaces might be critical locations for dissolved organic matter transformations. Here we experimentally study microbial and nonbiological processing of dissolved organic matter when anoxic mire-waters are aerated. We also assess how particles found in the peat-water may stimulate these processes. Our results suggest significant nonbiological particle formation and modification of the dissolved organic matter pool when anoxic waters from peatlands are first delivered to streams. In addition, we find that natural particles are important stimulators of these processes. We conclude that upstream systems are important and overlooked sites of dissolved organic matter processing in boreal freshwater systems.

©2020. The Authors.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

1. Introduction

Peatlands of the northern hemisphere store one third of the global soil carbon (C) pool (e.g., Gorham, 1991), and are highly sensitive to climate change (e.g., Freeman et al., 2001). A fraction of this stored C is transported from peatlands to adjacent streams and lakes in forms of inorganic carbon (IC) and organic carbon

Resources: Karólína Einarsdóttir, Dolly Kothawala, Ryan A. Sponseller, Lars J. Tranvik

Supervision: Dolly Kothawala, Ryan A. Sponseller, Lars J. Tranvik

Visualization: Karólína Einarsdóttir, Katrin Attermeyer, Jeffrey A. Hawkes, Dolly Kothawala, Ryan A. Sponseller, Lars J. Tranvik

Writing – original draft: Karólína Einarsdóttir

Writing – review & editing: Karólína Einarsdóttir, Katrin Attermeyer, Jeffrey A. Hawkes, Dolly Kothawala, Ryan A. Sponseller, Lars J. Tranvik

(OC) (Dinsmore & Billett, 2008; Laudon et al., 2011; Leach et al., 2016). Hence, in addition to being a sink for atmospheric C (e.g., Nilsson et al., 2008), peatlands are also major sources of C to inland waters, influencing downstream ecosystems and water quality (Curtis, 1998; Köhler et al., 2013; Seekell et al., 2015). While the roles of peatlands in the broader C cycle are widely accepted, and their contributions to C loading downstream well studied, the biotic and abiotic mechanisms regulating the fluxes and speciation of C across the peat-stream interface need further attention (Tank et al., 2018).

Headwater streams make up 90% of the channel length of boreal river networks (Bishop et al., 2008) and are the initial recipients of terrestrial organic matter (OM) supplied to inland waters. Still, these small streams are not well integrated into global estimates of export and fate of terrestrial OM (Drake et al., 2018). Given that terrestrial dissolved OM (DOM) may become highly reactive upon exposure to oxygen at soil-water interfaces (Einarsdottir et al., 2017; Hutchins et al., 2017; McClain et al., 2003), headwaters are potentially key sites for OM removal. For example, floods in northern temperate and boreal landscapes can supply streams with bioavailable DOM (Berggren et al., 2009; Fellman et al., 2014) that supports elevated rates of microbial respiration (Demars, 2019; Lupon et al., 2019). However, for streams draining peatlands, these responses may be constrained by the high degree of DOM recalcitrance to biodegradation (Ågren et al., 2008; Berggren et al., 2009; M. Chen & Jaffé, 2014). Indeed, others have argued that headwater streams are passive conveyers of DOM, due to short water retention times that allow only limited degradation in transit (Kothawala et al., 2015), especially during storm events (Raymond et al., 2016). Largely overlooked in this debate is abiotic processing of DOM that may take place in headwater environments. Upon seepage through soil-stream-interfaces, anoxic peat-water is exposed to oxygen that may trigger oxidation mechanisms and prompt selective removal of the DOM that forms to particles (POM) by, e.g., flocculation, adsorption, and coprecipitation with oxidizing iron (Huang et al., 2019; Liao et al., 2017; Riedel et al., 2013).

In boreal landscapes, headwater streams often emerge from gently sloping, iron- and organic-rich mires (poor fens) with pH 4.3–5.5 (Brinson, 1993; Rydin & Jeglum, 2013). Peat soils are generally waterlogged and water is continuously discharged from the mire to the stream (Brinson, 1993). When oxygen is absent, ferric iron (Fe (III)) is microbially reduced to soluble ferrous iron (Fe (II)) (Lovley & Phillips, 1986). During this dissimilatory iron reduction, organic species may also become soluble under anoxic conditions, resulting in elevated DOM concentrations in mire waters (Chin et al., 1998; Knorr, 2013; Pan et al., 2016; Peiffer et al., 1999). Upon aeration of mire-water, e.g., when discharged to streams, Fe (II) is reoxidized to insoluble Fe (III), which may promote coflocculation or coprecipitation of DOM (Huang et al., 2019; Liao et al., 2017; Riedel et al., 2013). However, since high proportion of Fe (II) (and Fe (III)) in peat soil is complexed by DOM, iron may escape full oxidation and still be in the water as a colloid (Kügler et al., 2019; Neubauer et al., 2013; Peiffer et al., 1999). The solubility and the redox potential of iron species are very dependent on pH, as well as temperature and ion strength (Morgan & Lahav, 2007). Hence, the significance of DOM and dissolved iron that are transported from mires to headwater streams may depend on pH and temperature and oxygen conditions in the mire (Hurt, 2004; Mitchell & Branfireun, 2005), but also shift abruptly when these water are supplied to open channels.

Suspended organic particles (POM) originating from peat (peat-particles) may also alter the fluxes and the fate of mire-derived OM. POM can be found in high concentration in mire waters (Tank et al., 2018), and in streams during storm events (Bilby & Likens, 1979; Correll et al., 2001; Jung et al., 2014; Wallace et al., 1995). Particle-attached microbes (biofilms) are known to be more efficient at degrading OM when compared to free-living microbes (Bell & Albright, 1982; Tranvik & Sieburth, 1989). Indeed, in boreal freshwaters, enhanced microbial OM degradation on particles suggests that such biofilms are very biogeochemically active (Attermeyer et al., 2018). Peat-particles partly consist of extracellular polymeric substances (EPSs) (Attermeyer et al., 2019; Tisdall, 1994) that are adhesive and promote DOM adsorption, and biofilm development (Passow, 2002; Tisdall, 1994; Xu et al., 2011), and thus can enhance microbial processing of OM, especially under oxic conditions (Starkey & Karr, 1984). EPSs can adsorb to clay minerals, including metal oxides (e.g., iron oxides) that are also important sorbents for DOM (Al-Sid-Cheikh et al., 2015; Mikutta et al., 2006). Depending on extrinsic properties (i.e., pH and ionic strength) and the nature of the sorbent (i.e., metal or organic particles), the adsorption (physisorption and chemisorption) mechanism may be selective on the sorbate (i.e., DOM species) (Sollins et al., 1996). For example, DOM that associates with iron oxides is mostly nitrogen-poor aromatic forms (Kleber et al., 2015) that may therefore have relatively high C:N ratio compared to EPS aggregates, which are more prone to adsorb N-rich species, such as

proteins and nucleic acids, along with inorganic N-ions (Simon et al., 2002; Wingender et al., 2012). These differences suggest that the mechanisms of particle formation could have important impacts on the residual properties of DOM as well as on the fate of OM downstream, either by favoring microbial uptake and mineralization or stimulating preservation and burial of OM.

In this experimental study, we asked how transitions from anoxic to oxic conditions influence the biotic and abiotic processing of DOM (e.g., at mire-stream interfaces) and how peat-particles may promote such processing. We answered these questions by simulating the process of aeration at the mire-stream interface in the lab. Specifically, we incubated unfiltered (with peat-particles) and filtered water (without peat-particles), collected from sloping mire during a dry period when the mire water was stagnant, anoxic, and highly concentrated with DOM and dissolved iron. We assessed the contribution of POM formation (flocculation and coprecipitation with oxidized iron and adsorption to peat-particles) and microbial degradation to DOM removal, as well as associated changes in DOM molecular composition upon aeration of the water. We hypothesized that a substantial fraction of DOM would be lost upon aeration, mainly via flocculation and coprecipitation with oxidized iron, but also due to biodegradation. Second, given that peat-particles may contain adhesive biofilms and clay minerals, we expected that particles would adsorb DOM, and stimulate biodegradation upon aeration. Lastly, we anticipated that the composition of DOM and POM pools would change selectively depending on the mechanism driving OM transformations.

2. Methods

2.1. Study Area

The study was carried out in a sloping mire (classified as a poor valley fen, Rydin & Jeglum, 2013) that drains into a small headwater stream (Figure 1). This mire is located in the boreal zone of south-central Sweden (59°51'70"N, 15°11'40"E), and is 1 ha in area with a slope of 2–3°. The 25 ha catchment of the mire consists of forest (90%) and mire (10%, Figure 1). This forest is dominated by Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*), and the dominant vegetation in the peatland is *Sphagnum* spp. and *Carex* spp., but *Picea abies*, *Vaccinium* spp., *Juncus* spp., and *Polytrichum* sp. are common on hummocks. The thickness of the peat soil varies from 0.5 to 1 m, and is deepest in the center of the mire. The main soil types of the catchment are brown forest soil and podzols lying atop Svecofennian intrusive rock, which is rich in iron and manganese oxides (Stephens, 2009). According to climate classification, the area is located on the boundaries of Dfb (cold summer) and Dfc (warm summer) (Beck et al., 2018). Mean annual temperature for the area is 4.5°C (−5.5°C for January and 15°C for July) and annual mean precipitation is 900 mm for the years 1961–1990 (Swedish Meteorological and Hydrological Institute, SMHI). The pH of the mire-water varies over the year from 4.4 to 4.8 and has a low electrical conductivity (25–45 $\mu\text{S}/\text{cm}$).

2.2. Field Sampling

On 5th August 2017, when the mire-water had been anoxic and stagnant or slowly flowing for a month, water samples were collected for the experiment with a peristaltic pump (Masterflex, E/S portable sampler, Cole Parmer Instrument Company) from two water-sampling tubes, which were located approximately 2 m from the mire-stream interface. The tubes were perforated with two 5 mm diameter holes at 1 cm increments from the surface to the bottom (~65 cm depth) so that water was collected from all depths of the organic soil. Water samples were collected in seven 2 L glass bottles (pre-acid washed and combusted at 450°C). Prior to sampling, water was pumped at a low rate to flush out of the hosing system and to dispose of stagnant water within the sampling tube. The pumping continued at a low rate to minimize the risk of aerating water flowing into the tube from the peat soil. To fill each bottle, a hose from the peristaltic pump was placed to the bottom of the bottle, and the bottle was overfilled with about 300 ml to minimize oxygen contamination before it was closed, headspace free, with cap containing aluminum covered septa. In addition, 300 ml of water sample were taken from the stream approximately 50 m downstream from the mire-stream interface, to use as a microbial inoculum for the experiment. The stream sample was filtered through precombusted GF/F filter (Whatman) and stored under dark and cold (4°C) conditions. For acclimatization of the inoculum, the stream sample stood in darkness at 15°C for 1 day prior to the experiment. All mire sample bottles were stored at 4°C in the dark, which should minimize microbial degradation, and were all completely anoxic prior to the experiment that took place 4 weeks from the date of collection. Although all precautions were taken to avoid aerating the water

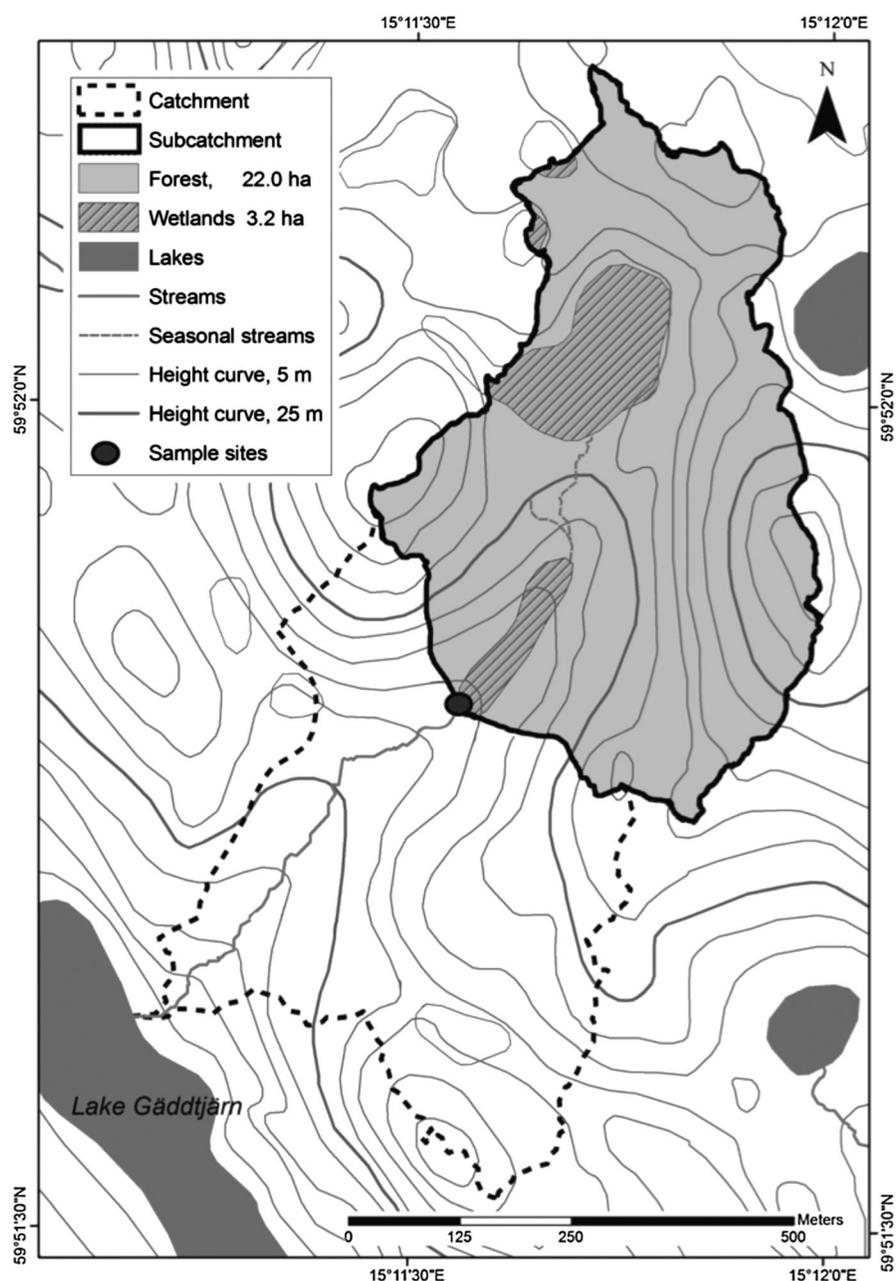


Figure 1. The map shows the catchment of the headwater stream. The solid line (and shaded area) indicates the catchment area that drains to the sloping mire. ©Lantmäteriet, i2012/921.

during and after the sampling, it is nonetheless possible that sample water was slightly oxygenated during this process. In the supporting information, results from this study and a pilot-study, which was conducted just 4 days after sampling, are compared and discussed. Briefly, this comparison shows similar initial conditions for DOC and total Fe and indicates that biases due to aeration upon sampling and 4 weeks of water storage before the experiment were unlikely to influence our results (see SI, Figure S2).

2.3. Incubation Experiment

A full-factorial experiment was conducted to test the influence of particles and oxygen on DOM in mire water, resulting in four treatments: (a) anoxic water with peat-particles (Anox/Unfilt), (b) aerated water

with particles (Ox/Unfilt), (c) anoxic water without peat-particles (Anox/Filt), and (d) aerated water without peat-particles (Ox/Filt). To ensure that samples maintained anoxic conditions, all bottles were placed in a N₂ gassed glovebox during initial stages of the experiment. From each of the four 2 L mire-water bottles, one 250 ml incubation bottle was prepared for each treatment, resulting in four replicates per treatment, 16 bottles in total (see SI, Figure S3).

To keep the water anoxic, all the incubation bottles were prepared in a glovebox. All water was sieved through a plankton-net (300 μm) to remove macrofauna and larger particles. For treatments without peat-particles, half of the sieved water was filtered through precombusted GF/F filters (Whatman, 47 mm diameter, nominal pore size 0.7 μm). After filtration, both water with peat-particles (only sieved) and without peat-particles (filtered) were sampled to obtain initial values of chemical parameters, composition of DOM, and concentrations of dissolved and particulate OCs (DOC and POC) and particulate nitrogen (PN), along with dissolved iron (Fe (III) and Fe (II), see section 2.5).

For anoxic treatments, eight 250 ml glass bottles were completely filled up resulting in a volume of ca 320 ml per bottle. Four of these had peat-particles (Anox/Unfilt) and the other four were without peat-particles (Anox/Filt). Before closing the bottles airtight and without any headspace, 20 ml samples were taken from each bottle for analysis of IC and 10 ml were taken for measuring partial pressure of CO₂ (pCO₂) (see section 2.4), spiked with a 10 ml inoculum from the stream water, and completely filled up again with treatment water.

For oxic treatments, ~400 ml of water was poured into eight 1 L glass bottles, so there was plenty of headspace, four with peat-particles (Ox/Unfilt) and four without peat-particles (Ox/Filt). These bottles were transferred from the glovebox to an incubation room that maintained the temperature at 15°C. To aerate the water, the bottles were opened several times to exchange air and introduce oxygen and then left on a rolling device in between. The bottles had a sensor spot (PreSens SP-PSt3, Regensburg Germany) to monitor the dissolved oxygen concentration during this period. Aeration proceeded for several hours depending on replicates (see SI, Figure S4), at which point concentrations were ~9 mg O₂/L. After aeration, samples for dissolved iron (see section 2.4) were taken from each bottle and then the aerated water was transferred into 250 ml incubation bottles. As above, each incubation bottle was sampled for IC and pCO₂ (see section 2.4), spiked with 10 ml of inoculum from the stream, and any remaining volume was replaced with water from the corresponding treatment, before capping them without headspace. It should be noted that during aeration, substantial amount of CO₂ was degassed from the bottles, but the loss of CO₂ was comparable to in situ measurements of the stream water and riparian mire water (see SI, Table S3).

Prior to starting the incubation, all anoxic bottles were taken out of the glovebox, and all incubation bottles (oxic and anoxic, 16 bottles in total) were put on the rolling device to simulate the stream flow and keep particles in solution, which is important for OM metabolism (Jarvis et al., 2005; Ward et al., 2018). The bottles were incubated for 5 days in the dark at 15°C, which was similar to the temperature of the stream at the sampling date. All incubation bottles were equipped with oxygen sensor spots (PreSens SP-PSt3, Regensburg, Germany) to allow for in situ measurements of oxygen concentrations in the beginning and the end of the incubation, and frequently (two times per day) during the incubation. All bottles were closed with airtight caps containing PTFE coated silicone septa covered with precombusted aluminum foil.

When the incubation was finished, anoxic bottles were transferred into the glovebox to sample chemical parameters (see section 2.5), while aerated bottles were sampled directly in the incubation room. Prior to the experiment, all plastics, silicon, and glassware that was used for the experiment and the sampling was acid washed (10% HCl) for 24 hr and soaked in deionized water for another 24 hr. Additionally, the acid washed glassware, GF/F filters, and aluminum foil (to cover the septa) were combusted at 450°C for 4 hr. Pictures were taken of the bottles before and after aeration period and again after 5 days of incubation (see SI, Figure S1), which show clear changes in color of the water, due to oxidation/hydrolysis of the iron.

2.4. Sampling and Analyses of Chemical Parameters

To sample DOC concentration, dissolved iron species, POC, PN, and DOM quality, 60 ml syringes were used and the treatments water was filtered through precombusted GF/F filters (Whatman, 25 mm diameter, pore size of approximately 0.7 μm) inserted in a filter holder that was attached to the syringe. The filtered volume

was recorded and the filters were dried and stored in a desiccator until analysis of concentration of POC and PN that was used to calculate the molar C:N ratio of the particles. To measure the concentration of POC and PN, the dried GF/F filters were packed into tin capsules and then analyzed on an Elemental Combustion System (Costech Instruments, Cernusco s/Nav., Italy).

The concentration of DOC was determined within 12 hr of sampling on a high sensitivity total carbon analyzer (Sievers M9 Laboratory Analyzer, GE Analytical Instruments, Boulder, Colorado, United States) with a precision of the analytical method of <1% relative standard deviation and an accuracy of $\pm 2\%$. Dissolved iron species (Fe (II) and Fe (III)) were analyzed and calculated according to the Ferrozine method described by Viollier et al. (2000) within 15 min of sampling. Absorbance at 562 nm was recorded on a spectrophotometer (UV/Vis Spectrometer Lambda 40, Perkin Elmer, Waltham, United States). Due to high concentration of DOC and dissolved iron, we diluted samples four times with MilliQ water. Before diluting anoxic samples, the MilliQ water was purged with nitrogen gas to remove any oxygen from the water and anoxic samples were diluted in the glovebox. Prior to analysis of dissolved iron in anoxic samples, ferrozine was added to samples inside the anoxic glovebox. To determine microbial respiration, IC was analyzed at the start and the end of the incubation. Bubble free samples were taken with a 20 ml syringe with attached tubing, and injected carefully into 17 ml glass vials by placing the tubing on the bottom, overfilling them, and closing without any headspace. Right after sampling of the incubation bottles, the IC concentration was analyzed using a high sensitivity total carbon analyzer (Sievers M9 Laboratory Analyzer, GE Analytical Instruments, Boulder, Colorado, United States). In addition to IC, $p\text{CO}_2$ was analyzed with an Infrared Gas Analyzer (EGM-3 and EGM-4, PP Systems). Ten milliliters of water was collected headspace and bubble free with 20 ml syringe that was closed with a three-way stopcock. The sample water was then shaken with 10 ml of N_2 gas for 1 min and the headspace was transferred to a second syringe that was directly injected into the gas analyzer.

To measure the composition of ionizable DOM, samples were analyzed using liquid chromatography-electrospray ionization-diode array detection-mass spectrometry (LC-DAD-ESI-MS) method as in Hawkes et al. (2018). Mire samples were already sufficiently high in DOC concentration for injection onto the LC-DAD-ESI-MS without concentration. Formic acid was added (25 μl 10% solution) to 475 μl of solution in order to protonate organic acids, and to improve retention on the reversed-phase column. The column was a polymeric polystyrene/divinylbenzene (150 \times 1.0 mm, 3 μm bed size, 100 \AA pore size; PLRP-S, Agilent), connected to an Agilent 1100 High Pressure Liquid Chromatography (HPLC). Mobile phase A was 5% acetonitrile in 0.1% formic acid, 0.05% ammonia (ammonium formate buffered to pH 3.35), mobile phase B was acetonitrile. Eighty microliters sample was injected, and was separated into three broad fractions as in Hawkes et al. (2018)—poorly retained material, material eluted by 20% mobile phase B, and hydrophobic material eluted by >45% B. The eluting material was detected by a diode array detector (DAD) at 254 nm with 410 nm as a reference (Agilent 1100) and Orbitrap mass spectrometer (LTQ Velos, Thermo Fisher), operated in negative mode (-3.1 kV). Ions were detected from 150–1,000 Da, and the spectra were internally calibrated and filtered for noise.

2.5. Data Analysis and Calculations

2.5.1. Quantity and Quality of POM Forming With Iron and Peat-Particles

One of the aims of this study was to estimate the quantity and the quality of the POM that generated from DOM after aeration, and 5 days of incubation on the rolling device. We consider there was a negligible amount of particulate material at the start of the incubation for the treatment with filtered water, therefore POM that was observed in the end of the experiment was formed by coprecipitation with iron oxides upon aeration, and flocculation. In the unfiltered treatment, where the peat-particles were present at the start of the experiment, we assume that POM not generated via coprecipitation with iron oxides must have adsorbed to the peat-particles. It should be noted that even though these two POM-forming processes are considered separately here, we understand that they very likely interacted in the unfiltered treatment, such that several mechanisms of DOM retention are occurring (including coprecipitation, aggregation, and adsorption). We consider that DOM adsorption to particles can occur via weaker physisorption (e.g., van der Waals forces) or chemisorption (e.g., ligand exchange) to mineral surfaces.

To calculate how much POC was formed upon the incubation in the treatment that contained peat-particles (Ox/Unfilt), the initial concentration of POC was subtracted from the concentration that was measured in the end of the experiment. Under the assumption that the coprecipitation of Fe-DOM and subsequent flocculation are the same in the filtered and unfiltered treatment, we estimated how much POM was formed via DOM adsorption to peat-particles. To do this, the observed POC formation from the filtered treatment (Ox/Filt) was subtracted from that formed POC in the unfiltered treatment (Ox/Unfilt).

$$\text{POC}_{\text{Unfilt/Peat}} = \Delta\text{POC}_{\text{Unfilt}} - \Delta\text{POC}_{\text{Filt/Fe}}, \quad (1)$$

where $\Delta\text{POC}_{\text{Unfilt}}$ is the generated POC during the incubation period in the aerated treatment with peat-particles (Ox/Unfilt), $\Delta\text{POC}_{\text{Filt/Fe}}$ is the POC formed in the aerated treatment without peat-particles (Ox/Filt), and $\text{POC}_{\text{Unfilt/Peat}}$ is the POC formed via adsorption to peat-particles in aerated treatment with peat-particles (Ox/Unfilt).

To assess the quality of the POM that was formed with iron precipitates, the molar C:N ratio of particles was calculated from POC and PN values of initial peat-particles and particles generated in all treatments during the incubation (except in Anox/Filt). The molar C:N ratio of POM generated by flocculation and coprecipitation with iron was supposed to be similar in both oxic treatments (Ox/Unfilt and Ox/Filt). Therefore, the concentration of PN formed in the treatment without peat-particles (Ox/Filt) was used to estimate how much of the measured PN in Ox/Unfilt was associated with peat-particles:

$$\text{PN}_{\text{Unfilt/Peat}} = \text{PN}_{\text{Unfilt}} - \text{PN}_{\text{Filt/Fe}}, \quad (2)$$

where $\text{PN}_{\text{Unfilt/Peat}}$ is the concentration of N retained on peat-particles, $\text{PN}_{\text{Filt/Fe}}$ is N that flocculated or coprecipitated with iron, and $\text{PN}_{\text{Unfilt}}$ is the concentration all POM in the treatment with peat-particles (Ox/Unfilt).

2.5.2. Microbial Respiration and Nonrespiratory Oxygen Removal

Oxygen consumption via microbial respiration was estimated during the incubation period for aerated treatments (Ox/Unfilt and Ox/Filt). A respiratory quotient of 1 was used to estimate O_2 loss from IC (CO_2) production. IC increase upon incubation (ΔIC) was calculated and converted to moles to estimate the amount of O_2 consumed by microbial respiration ($\Delta\text{O}_{2-\text{res}}$):

$$\Delta\text{IC} = \Delta\text{O}_{2-\text{res}}. \quad (3)$$

Then the microbial respiration ($\Delta\text{O}_{2-\text{res}}$) was subtracted from the measured oxygen consumption ($\Delta\text{O}_{2-\text{total}}$) to get the amount of oxygen that was lost via nonrespiratory processes ($\text{O}_{2-\text{non}}$):

$$\text{O}_{2-\text{non}} = \Delta\text{O}_{2-\text{total}} - \Delta\text{O}_{2-\text{res}}. \quad (4)$$

2.5.3. Molecular Composition of DOM Using LC-DAD-ESI-MS

For detecting instrumental noise, the data were screened in each transient by calculating the 95th percentile of peaks with mass defect of 0.6–0.8 and then intensities below this value by zero were replaced. Formulas in each transient were assigned as described previously (Hawkes et al., 2018), including all CHO formulas up to C40 H80 O40, one nitrogen, one sulfur, and one 13C. Only one of N, S, or 13C was allowed in any formula. Assignments were allowed if mass error was less than 1.5 ppm. The assigned intensities in each of the three time windows were summed (hydrophilic, medium hydrophobic, and hydrophobic material). This resulted in a list of $9,000 \times 3$ matrix of formulas vs. retention fraction for further visualization and statistical analysis.

2.5.4. Aromaticity of DOM

To estimate the differences in aromaticity of DOM between treatments, C-normalized HPLC absorbance at 254 nm was calculated from the integrated absorbance₂₅₄ area (A_{254}^{min}) and the DOC concentration. Since Fe (III) may increase the intensity of absorbance₂₅₄ (Weishaar et al., 2003), a correction factor was applied as described in Poulin et al. (2014) for the absorbance₂₅₄ area. The C-normalized HPLC absorbance₂₅₄ (A_{254}/C) was calculated as

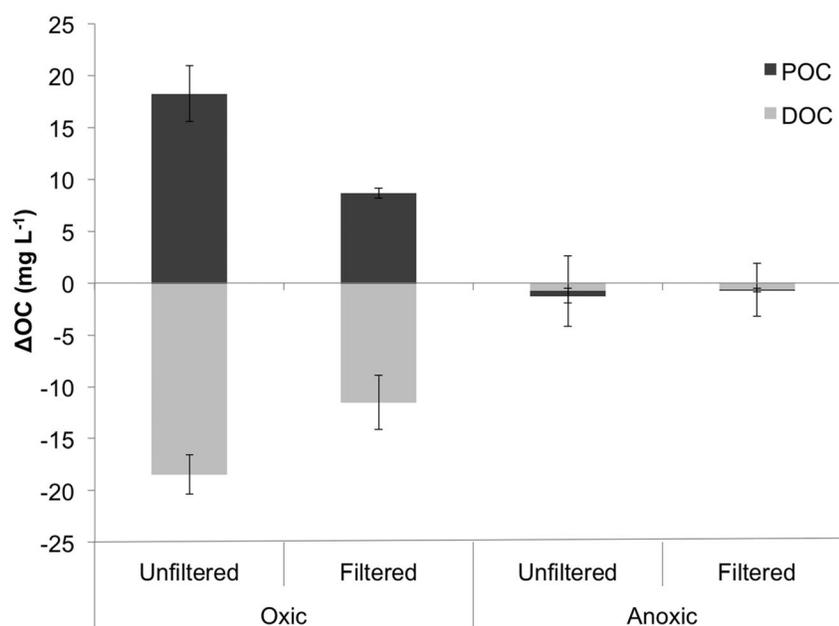


Figure 2. Changes in concentration of POC (dark gray) and DOC (light gray) upon the 5 days of incubation. Positive numbers indicate an increase and negative numbers a decrease. Error bars present SD ($n = 4$).

$$A_{254}/C = \frac{\bar{A}_{254} * l * t - 0.0653[\text{FeIII}]}{[\text{DOC}]}, \quad (5)$$

where A_{254} -bar is the average absorbance on Napierian scale, l is the length of the light travel in meters, and t is total elution time in minutes. Importantly, this approach of an aromaticity indication from HPLC absorbance is a qualitative, not a quantitative measure that we only used for comparing samples in this study, but not to other studies.

2.6. Statistical Analyses

To assess the differences in DOC, POC, C:N ratios, total dissolved iron, Fe (II), and Fe (III), the difference between the start and the end of the incubation period was calculated, and the changes were compared between all four treatments (Anox/Unfilt, Ox/Unfilt, Anox/Filt, and Ox/Filt). In addition, the C-normalized HPLC Absorbance between treatments that were observed after the incubation was compared. For those comparisons two-way analysis of variance (ANOVA) was conducted in JMP (version 13), followed by Tukey-Kramer HSD test to compare differences between all groups (see SI, Tables S1 and S2). Student's t test was used to check for significant differences of IC between aerated treatments (Ox/Unfilt and Ox/Filt), using JMP (version 13) (see SI, Table S2).

Statistical analyses of DOM composition were carried out in MATLAB (Version 2017b). The intersample dissimilarity of this 2-D matrix pairwise was assessed using the percent Bray-Curtis Dissimilarity scale (%BCD). Principle Coordinates Analysis (PCoA) were then conducted on the data using nonclassical multi-dimensional scaling of the %BSD distances, and Pearson's correlation between PCoA scores and each individual formula's normalized intensity was calculated. Correlations were considered significant if $p \leq 0.001$.

3. Results

3.1. Changes of Carbon Species

During the 5 days incubation of aerated mire water, we detected a substantial decrease in DOC concentration compared to water that was allowed to remain anoxic (Figure 2). Further, DOC loss under oxidic conditions was offset by an almost equivalent amount of POC formation (Figure 2). In addition, the concentration of IC did not change during anoxic conditions while it increased in oxidic treatments. The loss of DOC under oxidic conditions was significantly higher in Ox/Unfilt relative to Ox/Filt ($p < 0.0001$). In the

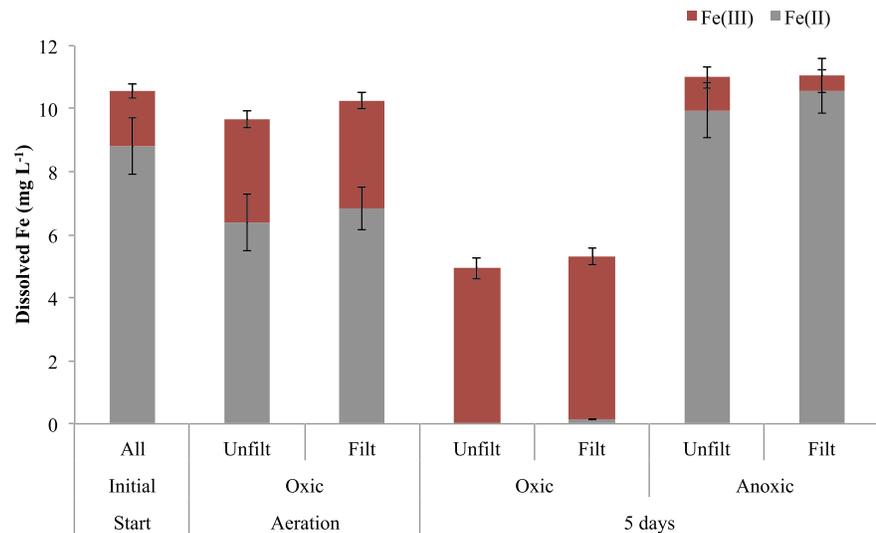


Figure 3. Concentration of dissolved iron. The bars present concentrations of total DFe, divided into Fe (II) (gray columns) and Fe (III) (red columns). Error bars present SD ($n = 4$).

Ox/Unfilt, the loss accounted for ~21.8% of the initial DOC pool (or 18.4 ± 1.9 mg/L), relative to only ~13.7% (11.5 ± 2.6 mg/L) in Ox/Filt (Figure 2). Similarly, IC and POC concentrations increased about twice as much in Ox/Unfilt compared to Ox/Filt (IC: 0.8 ± 0.1 mg/L and 0.4 ± 0.2 mg/L, $p = 0.01$, see SI, Figure S5; POC: 18.3 ± 2.7 mg/L and 8.6 ± 0.5 mg/L, $p < 0.0001$, Figure 2).

3.2. Changes of Iron Species

During the aeration of mire water prior to the incubation of oxic treatments, Fe (II) decreased from 8.8 ± 0.9 to 6.4 ± 0.9 mg/L ($p = 0.003$) in Ox/Unfilt and to 6.8 ± 0.7 mg/L ($p = 0.01$) in Ox/Filt (Figure 3). Fe (III) increased, respectively, from 1.7 ± 0.2 to 3.3 ± 0.3 mg/L ($p < 0.0001$) in Ox/Unfilt and to 3.4 ± 0.3 mg/L ($p < 0.0001$) in Ox/Filt. The concentration of total dissolved iron did not decrease significantly during the aeration time (Figure 3). However, at the end of the 5 days incubation for the oxic treatment, the total dissolved iron had decreased about 50%, from 10.5 ± 0.8 to 5.2 ± 0.3 mg/L ($p < 0.0001$) in Ox/Unfilt and 4.9 ± 0.3 mg/L in Ox/Filt (Figure 3), showing substantial transfer of dissolved iron to particulate form. The majority of the remaining dissolved iron was in the form of Fe (III), but Fe (II) was hardly measurable in either of the oxic treatments (<0.1 mg/L). The concentration of total dissolved iron did not change in anoxic treatments ($p = 0.9$), but a small portion of Fe (III) (0.7–1.2 mg/L) was reduced to Fe (II) during the incubation period (Figure 3). Both the loss of total dissolved iron and changes in iron species were very similar between Ox/Unfilt and Ox/Filt ($p = 0.97$, Figure 3).

3.3. Particle Formation and Composition

The estimated loss of DOC to POC due to association with dissolved iron in Ox/Unfilt was assumed to be similar as in Ox/Filt. This corresponded to a loss of ~9.5 mg DOC/L (mean of DOC loss and POC formation) flocculating and coprecipitating with iron, leaving ~8 mg/L (mean of DOC loss and POC formation) of DOC in Ox/Unfilt that was transformed to POC through adsorption to peat-particles during the incubation period.

The C:N ratio of peat-particles in the beginning of the experiment of unfiltered treatments (Anox/Unfilt and Ox/Unfilt) was 11.9 ± 0.9 and it did not change significantly upon 5 days incubation under anoxic conditions (Anox/Unfilt: 12.3 ± 0.6 , $p = 0.44$, Figure 4). The C:N ratio of particles that were formed via flocculation and coprecipitation with iron in Ox/Filt was more than twice as high, or 25.6 ± 2.2 ($p < 0.0001$). The C:N ratio of particles that were formed in Ox/Unfilt was also higher than the initial ratio (15.9 ± 1.6 , $p < 0.0001$). After subtracting the amount of particulate OC and N estimated to flocculate and coprecipitate with iron, the C:N ratio of the remaining POM was 13.8 ± 1.7 (comprising peat-particles with adsorbed OM).

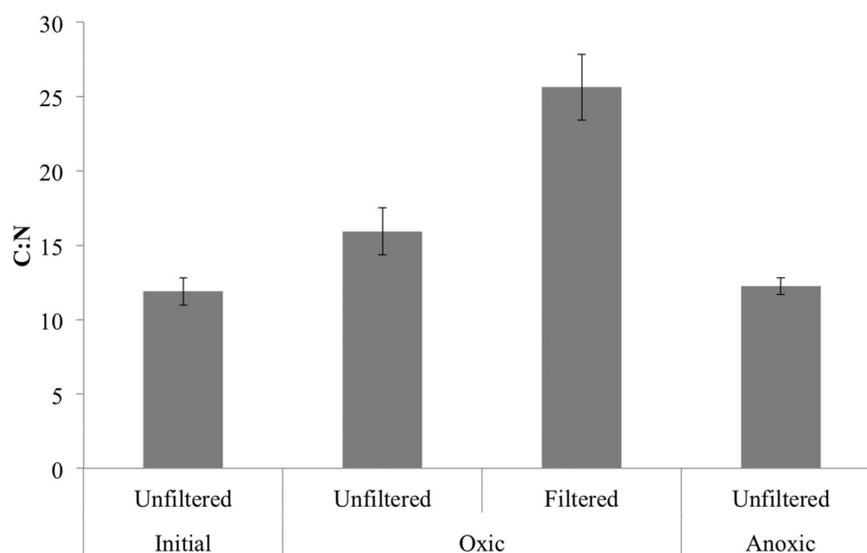


Figure 4. The molar C:N ratio of POM in the mire water at the start of the experiment and in response to different treatments. Initial sample represents the C:N ratio of peat-particles at the beginning of the incubation. Ox/Filt show C:N ratio of the POM-pool formed from DOM via coprecipitation with iron. C:N ratio of POM in Ox/Unfilt comprises a mixture of peat-particles, adsorbed OM, and iron-POM flocs. Anox/Unfilt shows the C:N ratio of the peat-particles when the water was remained anoxic. Error bars present SD ($n = 4$).

3.4. Molecular Composition of DOM

After the incubation, the UV-absorbing material showed an increased fraction of hydrophobic material in oxic samples compared to anoxic samples (fraction 3 in Figure 5, $p < 0.0001$). In contrast, anoxic samples contained more hydrophilic and amphiphilic material (fraction 1 and fraction 2, $p < 0.0001$, Figure 5). There was, however, no significant difference of retained material detected between the treatments with and without particles (fraction 1, $p = 0.96$; fraction 2, $p = 0.72$; and fraction 3, $p = 0.41$, Figure 5).

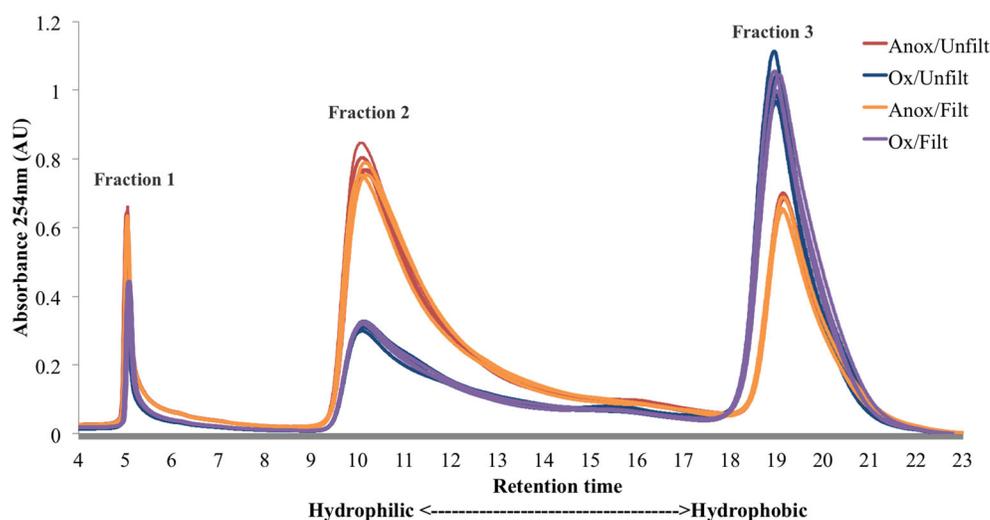


Figure 5. Reversed phase high pressure liquid chromatography (HPLC) separation with detection by diode array detector at 254 nm of DOM of all treatment after the 5 days incubation. Anoxic treatments are shown with red (Anox/Unfilt) and orange (Anox/Filt) lines; blue (Ox/Unfilt) and purple (Ox/Filt) lines represent oxic treatments. Retention time is a proxy for hydrophobicity of the DOM. $n = 4$ for each of the treatments with particles (Anox/Unfilt and Ox/Unfilt) and $n = 3$ for each of the treatment without particles (Anox/Filt and Ox/Filt).

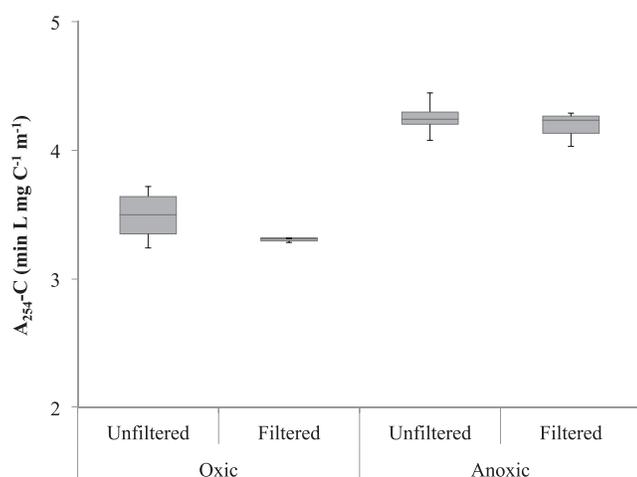


Figure 6. C-normalized HPLC absorbance (A_{254}/C) of all treatments after 5 days of incubation. The boxplot shows values of A_{254}/C that were calculated from an Fe (III) corrected integrated absorbance₂₅₄ area detected on HPLC-DAD, divided by the DOC concentration. The boxplot indicates median along with quartiles, and error bars present maximum and minimum values.

Comparing the C-normalized HPLC absorbance of the water after the incubation period showed that the aromaticity was significantly lower in aerated treatments ($p < 0.0001$), compared to samples that were anoxic (Figure 6). A trend toward lower aromaticity was detected in Ox/Filt when compared to Ox/Unfilt (Figure 6), but was not significant ($p = 0.43$). And there was no difference in aromaticity between Anox/Unfilt and Anox/Filt ($p = 0.83$, Figure 6).

The abundance of A_{254} active organic material was lower in oxic compared to anoxic samples (see SI, Figure S6a), while the MS trace was very similar between treatments (see SI, Figure S6b). There was a good correlation between DOC concentration and A_{254} (i.e., DOC loss is equivalent to loss of light attenuation, $r^2 = 0.89$), while DOC had little predictive power of LC-ESI-MS response ($r^2 = 0.15$, see SI, Figure S6c), suggesting minor impacts of DOC concentration on the quantity of the DOC that was ionized. LC-ESI-MS revealed, however, some significant difference within the ionizable DOM composition among treatments. The first component explained 52% difference among treatments, which was attributed to the difference between anoxic and oxic treatments. The second component explained 14% difference that referred to the difference between Ox/Unfilt and Ox/Filt (Figure 7a). Specifically, anoxic treatments were richer in some aliphatic forms (high H:C species). Additionally, they contained

more condensed aromatic forms (low H:C species) and more of those with unsaturated polyphenols (lignin-like forms, Figure 7b), suggesting removal of these organic species upon aeration. Within the oxic treatments, the chemical composition of DOM in Ox/Filt showed higher intensity of condensed aromatic forms (low H:C) than in Ox/Unfilt. Ox/Unfilt contained more unsaturated polyphenols along with some aliphatic forms (Figure 7c).

3.5. Oxygen Consumption

Upon the 5 days of incubation of oxic treatments, oxygen decreased by 5.0 ± 0.4 mg O_2/L in Ox/Unfilt and 3.6 ± 1.0 mg O_2/L in Ox/Filt treatments (Figure 8). We calculated the relative contribution of nonrespiratory oxygen removal and microbial respiration (measured from increased IC (CO_2)) of the measured oxygen. While oxygen loss via nonrespiratory oxidation was similar regardless of absence or presence of particles, there was a clear difference of microbial respiration between the treatments (Ox/Unfilt, ~ 2.1 mg O_2/L and

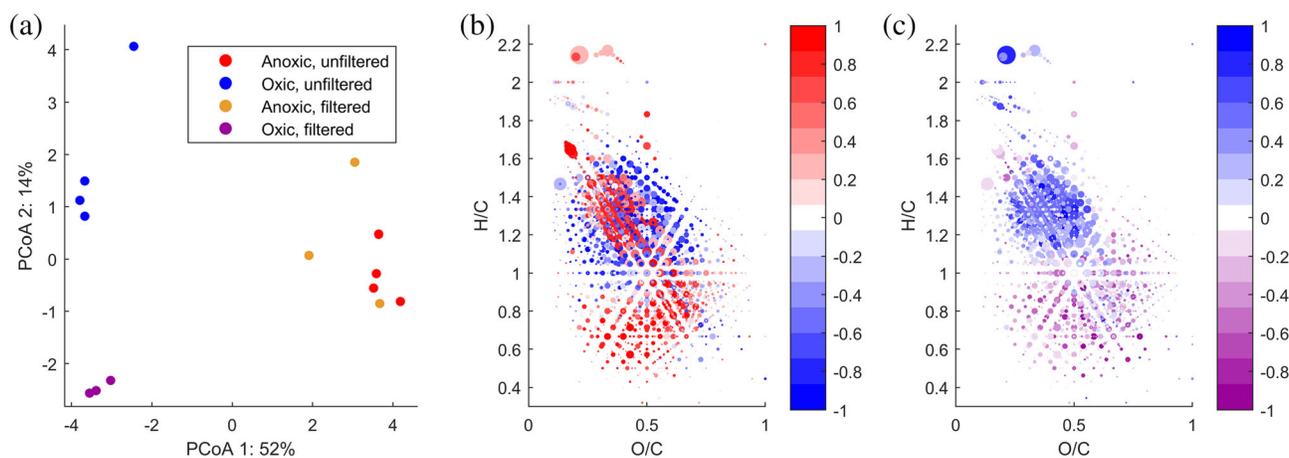


Figure 7. Qualitative differences in LC-DAD-ESI-MS detected DOM. (a) Principle coordinate diagram based on Bray-Curtis dissimilarities of the integrated MS signals across the whole chromatogram. (b–c) Van Krevelen diagrams showing detected formulas by O/C and H/C ratio. Pearson's correlation coefficients (color scale) of formula intensities and position along axes 1 and 2 (b and c, respectively). Red colored formulas were more abundant in the anoxic treatments, while blue-colored formulas became more relevant in oxic treatments (b). The purple-colored formulas were relatively more abundant in Ox/Filt, while blue-colored formulas became more relatively abundant in Ox/Unfilt (c). The point sizes indicate the intensity of ions.

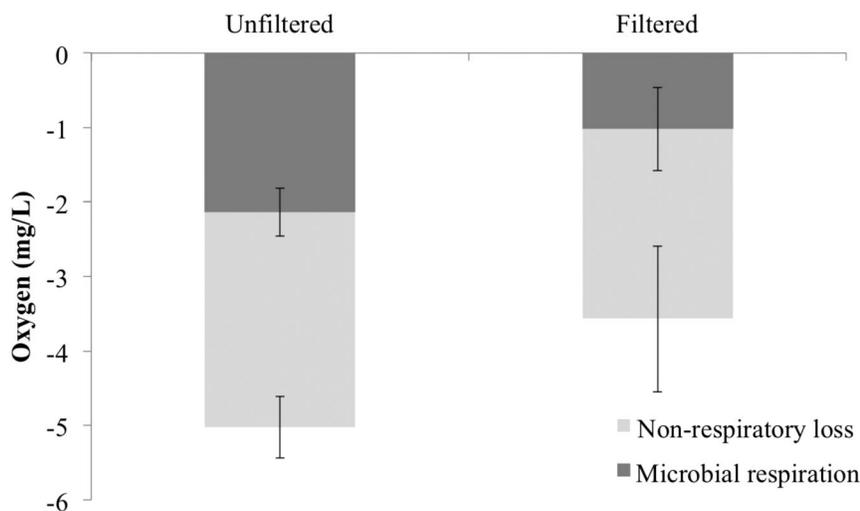


Figure 8. Calculated oxygen loss (negative values) during the 5 days of incubation of aerated samples: in presence of peat-particles (Unfiltered) vs. in absence of peat-particles (Filtered). The loss of microbial respiration (dark gray), calculated from the increase in IC (CO_2) during the incubation, and nonrespiratory loss (light gray). Error bars present SD ($n = 4$).

Ox/Filt, $\sim 1.0 \text{ mg O}_2/\text{L}$, Figure 8). The oxygen removal via nonrespiratory oxidation was therefore slightly higher than the removal due to microbial respiration in the presence of particles (Ox/Unfilt, $\sim 2.9 \text{ mg O}_2/\text{L}$), but almost three times higher in the absence of particles (Ox/Filt, $\sim 2.6 \text{ mg O}_2/\text{L}$).

4. Discussion

Headwater streams receive anoxic water from riparian zones and upstream mires. Upon exposure to oxygen at the soil-stream interfaces, OM carried with the water may undergo significant processing (McClain et al., 2003). Here we asked how DOM, POM, and iron of stagnant, anoxic mire-water change when the water becomes oxic upon discharge into a headwater stream. We show that DOM can form particles upon aeration due to flocculation and coprecipitation with oxidizing iron, as well as by adsorption onto initially available particles. Although particles provided important surfaces for DOM adsorption and enhanced microbial activity, biodegradation played only minor role for overall DOM loss and could only explain half of the oxygen consumption. The two different mechanisms that we suppose are driving the POM formation selected different DOM constituents and therefore resulted in particles with different chemical qualities. The POM formed presumably through association with iron was comprised of hydrophilic and amphiphilic N-poor aromatic forms, while the POM ostensibly formed by DOM adsorption to peat-particles mainly contained nonaromatic and more N-rich species. Aeration and DOM removal had also selective impacts on the remaining DOM pool, which became relatively more aliphatic and less aromatic. Overall, we suggest that abiotic transformation of selective DOM species, dissolved iron, and dissolved oxygen could be important and overlooked processes in headwaters draining peat-rich landscapes.

4.1. Abiotic Removal of DOM With Oxidizing Iron

While there is ongoing discussion regarding the importance of headwater streams as active processors of DOM, this debate has focused primarily on the potential significance of biological degradation (e.g., Berggren et al., 2009; Fasching et al., 2014) and photochemical processes (e.g., Hutchins et al., 2017; Köhler et al., 2002). Here we show that POM formation at the transition from anoxic soils to oxic stream conditions can be important for DOM removal and for the quality of DOM that ultimately reaches the stream. Specifically, 50% of the iron and 20% of the DOC were lost to particles within 5 days of our laboratory incubations. We detected that almost all of the Fe (II) was oxidized into Fe (III), half of which precipitated, presumably coprecipitating about 10–13% of the initial DOM. The remaining Fe (III) was retained in the water, most likely due to specific complexation with DOM, forming stabilized colloids (nanoparticles) (Kügler et al., 2019; Liao et al., 2017). Assuming the amount of POM formed via flocculation and

coprecipitation of iron oxides was similar in both treatments with and without peat-particles, about 50% of formed POM could be attributed to coprecipitation with iron and subsequent flocculation. Others have also shown significant association of OM and iron upon iron-oxidation, after aeration of anoxic water (Al-Sid-Cheikh et al., 2015; Peter et al., 2016; Riedel et al., 2013).

Several studies demonstrate that headwater streams receive highly reactive OM from forested riparian zones, particularly during higher discharge, and these inputs can be biodegraded rapidly (Berggren et al., 2009; Demars, 2019; Fellman et al., 2014). Yet during our 5 days incubation, microbial respiration was only responsible for 5% of the DOC removal (0.8 ± 0.1 mg/L DOC in water containing peat-particles and 0.4 ± 0.2 mg DOC in water without peat-particles) and was thus comparable to 0.5 ± 0.3 mg/L of DOC mineralized in filtered mire-water after 6 days of incubation, observed by Köhler et al. (2002). This reflects the relatively low susceptibility of mire DOM to microbial breakdown (Ågren et al., 2008; Berggren et al., 2009; M. Chen & Jaffé, 2014). While iron may stabilize soil OM under oxic condition (e.g., iron associated lignin), it may have negligible or even positive impacts on degradation in some organic-rich hydric soils (Emsens et al., 2016; Wang et al., 2019), and fluctuating redox conditions could also be important for bioavailability (C. Chen et al., 2020; Hall et al., 2015). This could suggest that iron may provide protection against biodegradation of OM in oxic waters and perhaps support a longer-term storage of OM in aquatic sediments (Lalonde et al., 2012). Overall, we suggest that abiotic processes linked to aeration at mire-stream interfaces could be important drivers of DOM removal, which may in turn be mobilized in particulate form, transported downstream, and/or preserved in sediments.

4.2. Peat-Particles Important Stimulators of DOM Processing

Upon aeration, we observed that the presence of peat-particles in the mire-water promoted additional loss of DOM. Both POM formation and microbial degradation of DOM was twice as high in the presence of peat-particles compared to the mire-water without peat-particles. Microbial activity and presence of microbial-produced EPSs have been linked to formation of POM under oxic conditions (He et al., 2016; Simon et al., 2002; von Wachenfeldt et al., 2009). In contrast, under anoxic conditions, microbial activity and EPS production are largely suppressed, and the adsorptive capacity is reduced (Sheng et al., 2008; Starkey & Karr, 1984), minimizing the role of particles as DOM sinks. Although we did not measure the concentration of EPS specifically, we suspect that EPS likely played an important role for both particle adsorption and microbial activity in the water with peat-particles upon aeration. EPS are ubiquitous features in soil (Tisdall, 1994) and high concentrations of EPS have been reported for peatlands (Attermeyer et al., 2019). These substances are hydrophobic and can be very adhesive, resulting in potent adsorbents for DOM, inorganic materials, and microbes (Passow, 2002; Tisdall, 1994; Xu et al., 2011).

EPSs are essential for biofilm development on particles (Simon et al., 2002), and such particle-attached biofilms may support more efficient OM degradation than free-living microbes (Bell & Albright, 1982; Tranvik & Sieburth, 1989). EPSs adsorb both inorganic ions and OM that provide energy and nutrients to microbes, allowing them to degrade nutrient-poor DOM that may adsorb to the particle surface (Paerl, 1975; Wotton, 1994). For example, a recent study reported that while particles account for only a small fraction of OM in boreal inland waters (5–15%), particle-associated degradation could explain 50% of the total OM removal (Attermeyer et al., 2018). This estimated contribution is similar to the proportion of particle associated DOM removal reported here. In light of our observations, and given that EPSs are ubiquitous in peat and inland waters with strong terrestrial connection (Attermeyer et al., 2019; Chateauvert et al., 2012), we hypothesize that EPSs play an essential role in DOM processing in headwaters and warrant further attention. Importantly, most incubation studies of DOM reactivity are performed using filtered water (e.g., Koehler et al., 2012; Vähätalo et al., 2010), and thus do not address the effect of particles. We show that more than twice the DOM was processed when initial particles were present in the incubation water, emphasizing that these particles should not be excluded when examining DOM processing.

4.3. Selectivity of Sorbents May Impact Quality and Fate of POM

One consequence of DOM flocculation, coprecipitation, and adsorption to peat-particles is the creation of organic particles that are biogeochemically reactive. The ultimate fate of these particles may be influenced by their intrinsic chemical properties, including their C:N ratio. Interestingly, we observed large differences in the C:N ratio between POM that was formed via iron association and formed via adsorption to peat-

particles. Although C:N ratios increased upon peat-particles adsorption of DOM (C:N ratio of ~14) compared to initial particles (C:N ratio of ~12), N was still in much higher abundance when compared to POM that coprecipitated with iron (C:N ratio of ~26). These observations, along with decreased DOM aromaticity upon aeration, are consistent with the idea that DOM associating with iron tends to be aromatic, N-poor OM (Kleber et al., 2015; Scheel et al., 2008), especially when concentration of humic substances are high (Avneri-Katz et al., 2017). In contrast, POM generated from adsorption to peat-particles must have been built from N-rich species and nonaromatic DOM since intensity of aromatic DOM did not decrease compared to the treatment without peat-particles.

The C:N ratio of POM may indicate its biodegradability and potential fate downstream (e.g., Gudasz et al., 2012; but see Reuter et al., 2020), and the C:N ratio of particles has been shown to increase upon microbial degradation for various surface waters along the land-ocean continuum (Attermeyer et al., 2018). We have proposed here that EPSs are a key contributor to peat-derived particles. The composition of EPS depends on the origin (i.e., cyanobacteria and diatoms), but comprises mainly carbohydrates and lipids, together with various N-rich species, such as proteins, amino acids, and inorganic N-ions, which could decrease their overall C:N ratio (Engel & Passow, 2001). However, the high variety of C:N ratios of POM generated from EPS aggregates does not necessarily depend on the EPS origin but much rather on the aggregate adhesion for N-species (Engel & Passow, 2001; Mari, 1999). In addition, the C:N ratio may also decrease upon microbial colonization and development of biofilms that immobilize nutrients (Pannard et al., 2016). In addition, EPSs are known to adsorb to minerals such as iron oxides that could favor a formation of biofilm and microbial activity, but too much iron could act as a shield that promotes steric hindrance (Hu et al., 2016), perhaps preserving the low C:N ratio of the POM. Based on the differences in POM quality that we observed between coprecipitation with iron oxide and adsorption to the peat-particles, we suggest that properties of the sorbents (e.g., iron oxides and adhesive EPS) are differentially selective in the removal of DOM. Hence, these differences could influence the fate and the function of the POM downstream, either by stimulating microbial uptake and DOM turnover or promote preservation of a fraction of the OM pool.

4.4. Selective Removal Leaves Behind Aliphatic and Hydrophobic Aromatic DOM

The processes of DOM removal and particle formation that takes place after aeration at the soil-stream interface leave behind a pool of DOM that ultimately makes its way downstream. In this sense, these transformations may also shape the eventual fate of DOM by increasing or decreasing its reactivity. After 5 days of incubation of aerated samples, our HPLC results revealed that UV-absorbing material decreased in the two most polar fractions and increased in the most hydrophobic fraction. Note that the hydrophobicity referred to is at pH < 3, as the samples were acidified with formic acid prior to analysis. The loss of UV absorption in the polar and midpolarity fractions indicates that the DOM that coprecipitated with iron was mainly hydrophilic and amphiphilic aromatic. In addition, we suggest that the Fe (III) which remained suspended in the aerated water upon oxidation of Fe (II) could be the cause of the increase in UV absorption in the hydrophobic fraction since unlike Fe (II), Fe (III) absorbs light at 254 nm (Doane & Horwath, 2010). Notably, the ESI-MS response of the last polarity fraction was very similar between anoxic and aerated samples (see SI, Figure S5b), supporting this possibility, but this hypothesis needs to be tested with further studies. Indeed, 50% of the initial dissolved iron remained suspended in the aerated water as Fe (III), most likely associated with DOM in colloidal forms. These colloids may be sensitive to electrostatic changes in the downstream environment, such as changes in pH and ionic strength (Vermeer et al., 1998), which could promote aggregation, flocculation, and sedimentation (Chandler, 2005; Demangeat et al., 2018; Jiang et al., 2017). Furthermore, Fenton-processes such as photo-reduction of Fe (III) upon exposure to light may also cause instability of such colloids, leading to dissolution and degradation of the colloidal OM (Minella et al., 2014).

LC-DAD-ESI-MS results showed similar trends of a loss of aromatic species upon aeration of anoxic water, and corresponded closely to previous studies showing loss of low H:C species, such as unsaturated polyphenols and highly condensed aromatic forms that are prone to associate with Fe (III) (Dadi et al., 2017; Riedel et al., 2013; Sodano et al., 2017). Unsaturated polyphenols and some aliphatic forms were dominant in the treatment with peat-particles, while condensed aromatic forms were more dominant in the filtered treatment. This could suggest a shift in the composition of the DOM pool upon aeration linked to presence of

peat-particles, and attributed to dynamics of dissolution-attachment processes of these specific species from POM, either promoted by microbial activity (He et al., 2016; Quigg et al., 2016; Zhou et al., 2019) or abiotic processes (such as ligands exchanges) (He et al., 2016; Kleber et al., 2015). Unfortunately, neither the HPLC-DAD nor the LC-DAD-ESI-MS results identified specific characteristics of DOM that were removed via peat-particles adsorption. Thus, we assume that the adsorbed material must have been poorly detectable via the method we used due to lack of light absorbance and polarity for ionization (Hawkes et al., 2019). In addition, we found that quantitatively, ESI-ionizable DOM was similar across a wide range of DOC concentrations, while UV-absorbing DOM differed substantially. The same was observed by Hawkes et al. (2019), who showed that terrestrial DOM could be separated into two pools of DOM: one that was UV-absorbing, and the other that was efficiently ionized and detected by ESI-MS. This result highlights the limitation of using only ESI-MS to examine changes in DOM composition, particularly in aquatic environments that are highly influenced by their terrestrial surroundings. However, we can conclude that the findings from our experiment suggest aeration dependent loss of DOM from anoxic mire-water not only constrains the quantity of DOM transported downstream, but also modifies the composition of DOM toward relatively more aliphatic and hydrophobic aromatic species.

4.5. Half of the Oxygen Consumption Driven by Nonrespiratory Factors

In addition to the influence on OM dynamics, nonrespiratory oxygen consumption processes may also represent an overlooked sink for oxygen when anoxic mire water is flushed into an oxic stream during storm events. Indeed, only about half of the dissolved oxygen loss in the treatment with peat-particles was due to microbial respiration, and even less in the treatment without peat-particles. There are a number of oxygen-sensitive species and processes that may react upon aeration of anoxic water. Besides Fe (II), Mn (II), and other reduced metal species, some organic species, such as quinones and phenols, get rapidly oxidized when exposed to oxygen (e.g., Lau & del Giorgio, 2020). In addition to these processes, nitrification of ammonium (NH_4^+) that has accumulated in anoxic mire-waters (e.g., Lupon et al., 2020) may also contribute to oxygen removal as flow paths traverse the mire-stream interface.

We suggest that when accumulated reduced material from hydric soil is supplied to streams, a substantial amount of oxygen could be removed due to nonrespiratory oxidation. This consumption could be relevant to studies of stream metabolism built on in situ oxygen measurements and the assumption that all oxygen removal occurs via biotic respiration (e.g., Marzolf et al., 1994; Torgersen & Branco, 2008). For example, increased oxygen consumption has been observed in headwater streams during elevated flow, and interpreted as microbial respiration as a result of lateral export of bioavailable DOM (e.g., Demars, 2019). However, it is also recognized that during high discharge, concentrations of oxygen sensitive species such as dissolved iron can rise in surface waters, being mobilized from saturated water of anoxic soils (Björnerås et al., 2017; Guan et al., 2016; Knorr, 2013) and these may rapidly react with dissolved oxygen.

Although our experimental design did not perfectly simulate the aeration process that takes place in the natural environment, or take into account the interaction with the streambed and the seeping water from the riparian zone, we think that the underlying processes are transferable to in situ conditions. Our experiment mimicked stream temperature, used turbulent mixing for aeration that may capture stream conditions, and included incubations with water spiked with a stream inoculum. Upon aeration, degassed CO_2 was similar to in situ CO_2 loss (see further SI, Table S3). Aeration may increase pH of mire water (e.g., Zak et al., 2004), but the slow iron oxidation rate during our experiment (see further SI, Figure S4) indicates that pH may only have increased slightly, or from ~ 4.7 to ~ 5 (Morgan & Lahav, 2007). Since many redox reactions are pH sensitive, a pH-shift upon aeration and subsequent mixing with stream water could additionally influence in situ oxygen losses. However, considering that pH of the mire was 4.6–4.8, we doubt that there were dramatic pH-shifts occurring upon aeration, and argue that the pH sensitive processes that we observed in the experiment are likely to happen downstream where the water increases in pH (>5). Thus, while it is challenging to extrapolate these laboratory incubations to the field, if rates of nonrespiratory oxygen removal are sufficiently high, these could lead to overestimates of microbial respiration in stream metabolism studies. We suggest that these processes merit further attention, particularly in mire-rich upland-catchments.

Data Availability Statement

Data sets for this research can be found on the openly available repository of Uppsala University (DiVA; <http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-423189>) under following ID: <http://uu.diva-portal.org/smash/record.jsf?pid=diva2%3A1477997>.

Acknowledgments

The study was financed by funds to L.T. from the Knut and Alice Wallenberg Foundation (KAW2013.0091) and the Swedish Research Council (2014-04264 and 2015-4870). K.E. acknowledges the Malméns Foundation and a funding from UVC, and K.A. acknowledges German Research Foundation (DFG, Research Fellowship AT 185/1-1). In addition, the authors would like to thank Christoffer Bergvall for technical laboratory support, Lilja Hrönn Fjölinsdóttir for field assistance, and Ellinor Ramberg for making the map.

References

- Ågren, A., Buffam, I., Berggren, M., Bishop, K., Jansson, M., & Laudon, H. (2008). Dissolved organic carbon characteristics in boreal streams in a forest-wetland gradient during the transition between winter and summer. *Journal of Geophysical Research*, *113*, G03031. <https://doi.org/10.1029/2007JG000674>
- Al-Sid-Cheikh, M., Pédrot, M., Dia, A., Guenet, H., Vantelon, D., Davranche, M., et al. (2015). Interactions between natural organic matter, sulfur, arsenic and iron oxides in re-oxidation compounds within riparian wetlands: NanoSIMS and X-ray adsorption spectroscopy evidences. *Science of the Total Environment*, *515–516*, 118–128. <https://doi.org/10.1016/j.scitotenv.2015.02.047>
- Attermeyer, K., Andersson, S., Catalán, N., Einarsdóttir, K., Groeneveld, M., Székely, A. J., & Tranvik, L. J. (2019). Potential terrestrial influence on transparent exopolymer particle concentrations in boreal freshwaters. *Limnology and Oceanography*, *64*(6), 2455–2466. <https://doi.org/10.1002/lno.11197>
- Attermeyer, K., Catalán, N., Einarsdóttir, K., Freixa, A., Groeneveld, M., Hawkes, J. A., et al. (2018). Organic carbon processing during transport through boreal inland waters: Particles as important sites. *Journal of Geophysical Research: Biogeosciences*, *123*, 2412–2428. <https://doi.org/10.1029/2018JG004500>
- Avneri-Katz, S., Young, R. B., McKenna, A. M., Chen, H., Corilo, Y. E., & Polubesova, T. (2017). Adsorptive fractionation of dissolved organic matter (DOM) by mineral soil: Macroscale approach and molecular insight. *Organic Geochemistry*, *103*, 113–124. <https://doi.org/10.1016/j.orggeochem.2016.11.004>
- Beck, H. E., Zimmermann, N. E., McVicar, T. R., Vergopolan, N., Berg, A., & Wood, E. F. (2018). Present and future Köppen-Geiger climate classification maps at 1-km resolution. *Scientific Data*, *5*(1), 1–12. <https://doi.org/10.1038/sdata.2018.214>
- Bell, C. R., & Albright, L. J. (1982). Attached and free-floating bacteria in a diverse selection of water bodies. *Applied and Environmental Microbiology*, *43*(6), 1227–1237. <https://doi.org/10.1128/AEM.43.6.1227-1237.1982>
- Berggren, M., Laudon, H., & Jansson, M. (2009). Hydrological control of organic carbon support for bacterial growth in boreal headwater streams. *Microbial Ecology*, *57*(1), 170–178. <https://doi.org/10.1007/s00248-008-9423-6>
- Bilby, R. E., & Likens, G. E. (1979). Effect of hydrologic fluctuations on the transport of fine particulate organic carbon in a small stream. *Limnology and Oceanography*, *24*(1), 69–75. <https://doi.org/10.4319/lo.1979.24.1.0069>
- Bishop, K., Buffam, I., Erlandsson, M., Fölster, J., Laudon, H., Seibert, J., & Temnerud, J. (2008). Aqua incognita: The unknown headwaters. *Hydrological Processes*, *22*(8), 1239–1242. <https://doi.org/10.1002/hyp.7049>
- Björnerås, C., Weyhenmeyer, G. A., Evans, C. D., Gessner, M. O., Grossart, H.-P., Kangur, K., et al. (2017). Widespread increases in iron concentration in European and north American freshwaters. *Global Biogeochemical Cycles*, *31*, 1488–1500. <https://doi.org/10.1002/2017GB005749>
- Brinson, M. M. (1993). *A hydrogeomorphic classification for wetlands (Wetlands Research Program Technical Report WRP-DE-4)*. Vicksburg, MS: U.S. Army Corps of Engineers Engineer Waterways Experiment Station. Retrieved from <https://apps.dtic.mil/docs/citations/ADA270053>
- Chandler, D. (2005). Interfaces and the driving force of hydrophobic assembly. *Nature*, *437*(7059), 640–647. <https://doi.org/10.1038/nature04162>
- Chateauvert, C. A., Lesack, L. F. W., & Bothwell, M. L. (2012). Abundance and patterns of transparent exopolymer particles (TEP) in Arctic floodplain lakes of the Mackenzie River Delta. *Journal of Geophysical Research*, *117*, G04013. <https://doi.org/10.1029/2012JG002132>
- Chen, C., Hall, S. J., Coward, E., & Thompson, A. (2020). Iron-mediated organic matter decomposition in humid soils can counteract protection. *Nature Communications*, *11*(1), 2255. <https://doi.org/10.1038/s41467-020-16071-5>
- Chen, M., & Jaffé, R. (2014). Photo- and bio-reactivity patterns of dissolved organic matter from biomass and soil leachates and surface waters in a subtropical wetland. *Water Research*, *61*, 181–190. <https://doi.org/10.1016/j.watres.2014.03.075>
- Chin, Y.-P., Traina, S. J., Swank, C. R., & Backhus, D. (1998). Abundance and properties of dissolved organic matter in pore waters of a freshwater wetland. *Limnology and Oceanography*, *43*(6), 1287–1296. <https://doi.org/10.4319/lo.1998.43.6.1287>
- Correll, D. L., Jordan, T. E., & Weller, D. E. (2001). Effects of precipitation, air temperature, and land use on organic carbon discharges from Rhode River watersheds. *Water, Air, and Soil Pollution*, *128*(1–2), 139–159. <https://doi.org/10.1023/a:1010337623092>
- Curtis, P. J. (1998). Climatic and hydrologic control of DOM concentration and quality in lakes. In D. O. Hessen, & L. J. Tranvik (Eds.), *Aquatic Humic Substances: Ecology and Biogeochemistry* (133rd ed., Vol. 133, pp. 93–104). Berlin: Springer-Verlag.
- Dadi, T., Harir, M., Hertkorn, N., Koschorreck, M., Schmitt-Kopplin, P., & Herzsprung, P. (2017). Redox conditions affect dissolved organic carbon quality in stratified freshwaters. *Environmental Science & Technology*, *51*(23), 13,705–13,713. <https://doi.org/10.1021/acs.est.7b04194>
- Demangeat, E., Pédrot, M., Dia, A., Bouhnik-le-Coz, M., Grasset, F., Hanna, K., et al. (2018). Colloidal and chemical stabilities of iron oxide nanoparticles in aqueous solutions: The interplay of structural, chemical and environmental drivers. *Environmental Science: Nano*, *5*(4), 992–1001. <https://doi.org/10.1039/C7EN01159H>
- Demars, B. O. L. (2019). Hydrological pulses and burning of dissolved organic carbon by stream respiration. *Limnology and Oceanography*, *64*(1), 406–421. <https://doi.org/10.1002/lno.11048>
- Dinsmore, K. J., & Billett, M. F. (2008). Continuous measurement and modeling of CO₂ losses from a peatland stream during stormflow events. *Water Resources Research*, *44*, W12417. <https://doi.org/10.1029/2008WR007284>
- Doane, T. A., & Horwáth, W. R. (2010). Eliminating interference from iron (III) for ultraviolet absorbance measurements of dissolved organic matter. *Chemosphere*, *78*(11), 1409–1415. <https://doi.org/10.1016/j.chemosphere.2009.12.062>
- Drake, T. W., Raymond, P. A., & Spencer, R. G. M. (2018). Terrestrial carbon inputs to inland waters: A current synthesis of estimates and uncertainty. *Limnology and Oceanography Letters*, *3*(3), 132–142. <https://doi.org/10.1002/lol2.10055>
- Einarsdóttir, K., Wallin, M. B., & Sobek, S. (2017). High terrestrial carbon load via groundwater to a boreal lake dominated by surface water inflow. *Journal of Geophysical Research: Biogeosciences*, *122*, 15–29. <https://doi.org/10.1002/2016JG003495>

- Emsens, W.-J., Aggenbach, C. J. S., Schoutens, K., Smolders, A. J. P., Zak, D., & van Diggelen, R. (2016). Soil iron content as a predictor of carbon and nutrient mobilization in rewetted fens. *PLoS ONE*, *11*(4), e0153166. <https://doi.org/10.1371/journal.pone.0153166>
- Engel, A., & Passow, U. (2001). Carbon and nitrogen content of transparent exopolymer particles (TEP) in relation to their Alcian Blue adsorption. *Marine Ecology Progress Series*, *219*, 1–10. <https://doi.org/10.3354/meps219001>
- Fasching, C., Behounek, B., Singer, G. A., & Battin, T. J. (2014). Microbial degradation of terrigenous dissolved organic matter and potential consequences for carbon cycling in brown-water streams. *Scientific Reports*, *4*(1), 1–7. <https://doi.org/10.1038/srep04981>
- Fellman, J. B., Spencer, R. G. M., Raymond, P. A., Pettit, N. E., Skrzypek, G., Hernes, P. J., & Grierson, P. F. (2014). Dissolved organic carbon biolability decreases along with its modernization in fluvial networks in an ancient landscape. *Ecology*, *95*(9), 2622–2632. <https://doi.org/10.1890/13-1360.1>
- Freeman, C., Evans, C. D., Monteith, D. T., Reynolds, B., & Fenner, N. (2001). Export of organic carbon from peat soils. *Nature*, *412*(6849), 785–785. <https://doi.org/10.1038/35090628>
- Gorham, E. (1991). Northern Peatlands: Role in the carbon cycle and probable responses to climatic warming. *Ecological Applications*, *1*(2), 182–195. <https://doi.org/10.2307/1941811>
- Guan, J., Yan, B., & Yuan, X. (2016). Variations of total dissolved iron and its impacts during an extreme spring flooding event in the Songhua River. *Journal of Geochemical Exploration*, *166*, 27–32. <https://doi.org/10.1016/j.gexplo.2016.04.003>
- Gudasz, C., Bastviken, D., Premke, K., Steger, K., & Tranvik, L. J. (2012). Constrained microbial processing of allochthonous organic carbon in boreal lake sediments. *Limnology and Oceanography*, *57*(1), 163–175. <https://doi.org/10.4319/lo.2012.57.1.0163>
- Hall, S. J., Silver, W. L., Timokhin, V. I., & Hammel, K. E. (2015). Lignin decomposition is sustained under fluctuating redox conditions in humid tropical forest soils. *Global Change Biology*, *21*(7), 2818–2828. <https://doi.org/10.1111/gcb.12908>
- Hawkes, J. A., Radoman, N., Bergquist, J., Wallin, M. B., Tranvik, L. J., & Löfgren, S. (2018). Regional diversity of complex dissolved organic matter across forested hemiboreal headwater streams. *Scientific Reports*, *8*(1), 16060. <https://doi.org/10.1038/s41598-018-34272-3>
- Hawkes, J. A., Sjöberg, R., J. P., Bergquist, J., & Tranvik, J. (2019). Complexity of dissolved organic matter in the molecular size dimension: Insights from coupled size exclusion chromatography electrospray ionisation mass spectrometry. *Faraday Discussions*, *218*, 52–71. <https://doi.org/10.1039/C8FD00222C>
- He, W., Chen, M., Schlautman, M. A., & Hur, J. (2016). Dynamic exchanges between DOM and POM pools in coastal and inland aquatic ecosystems: A review. *Science of the Total Environment*, *551*–552, 415–428. <https://doi.org/10.1016/j.scitotenv.2016.02.031>
- Hu, X., Chen, K., Lai, X., Ji, S., & Kaiser, K. (2016). Effects of Fe (III) on biofilm and its extracellular polymeric substances (EPS) in fixed bed biofilm reactors. *Water Science and Technology*, *73*(9), 2060–2066. <https://doi.org/10.2166/wst.2016.042>
- Huang, Z., Lv, J., Cao, D., & Zhang, S. (2019). Iron plays an important role in molecular fractionation of dissolved organic matter at soil-water interface. *Science of the Total Environment*, *670*, 300–307. <https://doi.org/10.1016/j.scitotenv.2019.03.214>
- Hurt, G. W. (2004). In D. Hillel (Ed.), *Hydric soils, Encyclopedia of Soils in the Environment* (Vol. 2, pp. 212–217). Amsterdam: Elsevier/Academic Press. <https://doi.org/10.1016/B0-12-348530-4/00030-8>
- Hutchins, R. H. S., Aukes, P., Schiff, S. L., Dittmar, T., Prairie, Y. T., & del Giorgio, P. A. (2017). The optical, chemical, and molecular dissolved organic matter succession along a boreal soil-stream-river continuum. *Journal of Geophysical Research: Biogeosciences*, *122*, 2892–2908. <https://doi.org/10.1002/2017JG004094>
- Jarvis, P., Jefferson, B., Gregory, J., & Parsons, S. A. (2005). A review of floc strength and breakage. *Water Research*, *39*(14), 3121–3137. <https://doi.org/10.1016/j.watres.2005.05.022>
- Jiang, L., Cao, S., Cheung, P. P.-H., Zheng, X., Leung, C. W. T., Peng, Q., et al. (2017). Real-time monitoring of hydrophobic aggregation reveals a critical role of cooperativity in hydrophobic effect. *Nature Communications*, *8*(1), 1–8. <https://doi.org/10.1038/ncomms15639>
- Jung, B.-J., Lee, J.-K., Kim, H., & Park, J.-H. (2014). Export, biodegradation, and disinfection byproduct formation of dissolved and particulate organic carbon in a forested headwater stream during extreme rainfall events. *Biogeosciences*, *11*, 6119–6129. <https://doi.org/10.5194/bg-11-6119-2014>
- Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., & Nico, P. S. (2015). Chapter one—Mineral-organic associations: Formation, properties, and relevance in soil environments. *Advances in Agronomy*, *130*, 1–140.
- 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. <https://doi.org/10.5194/bg-10-891-2013>
- Koehler, B., von Wachenfeldt, E., Kothawala, D., & Tranvik, L. J. (2012). Reactivity continuum of dissolved organic carbon decomposition in lake water. *Journal of Geophysical Research*, *117*, G01024. <https://doi.org/10.1029/2011JG001793>
- Köhler, S., Buffam, I., Jonsson, A., & Bishop, K. (2002). Photochemical and microbial processing of stream and soil water dissolved organic matter in a boreal forested catchment in northern Sweden. *Aquatic Sciences*, *64*(3), 269–281. <https://doi.org/10.1007/s00027-002-8071-z>
- Köhler, S. J., Kothawala, D., Futter, M. N., Liungman, O., & Tranvik, L. (2013). In-lake processes offset increased terrestrial inputs of dissolved organic carbon and color to lakes. *PLoS ONE*, *8*(8), e70598. <https://doi.org/10.1371/journal.pone.0070598>
- Kothawala, D. N., Ji, X., Laudon, H., Ågren, A. M., Futter, M. N., Köhler, S. J., & Tranvik, L. J. (2015). The relative influence of land cover, hydrology, and in-stream processing on the composition of dissolved organic matter in boreal streams. *Journal of Geophysical Research: Biogeosciences*, *120*, 1491–1505. <https://doi.org/10.1002/2015JG002946>
- Kügler, S., Cooper, R. E., Wegner, C.-E., Mohr, J. F., Wichard, T., & Küsel, K. (2019). Iron-organic matter complexes accelerate microbial iron cycling in an iron-rich fen. *Science of the Total Environment*, *646*, 972–988. <https://doi.org/10.1016/j.scitotenv.2018.07.258>
- Lalonde, K., Mucci, A., Ouellet, A., & Gélinais, Y. (2012). Preservation of organic matter in sediments promoted by iron. *Nature*, *483*(7388), 198–200. <https://doi.org/10.1038/nature10855>
- Lau, M. P., & del Giorgio, P. (2020). Reactivity, fate and functional roles of dissolved organic matter in anoxic inland waters. *Biology Letters*, *16*(2), 20190694. <https://doi.org/10.1098/rsbl.2019.0694>
- Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., et al. (2011). Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: The role of processes, connectivity, and scaling. *Ecosystems*, *14*(6), 880–893. <https://doi.org/10.1007/s10021-011-9452-8>
- Leach, J. A., Larsson, A., Wallin, M. B., Nilsson, M. B., & Laudon, H. (2016). Twelve year interannual and seasonal variability of stream carbon export from a boreal peatland catchment. *Journal of Geophysical Research: Biogeosciences*, *121*, 1851–1866. <https://doi.org/10.1002/2016JG003357>
- Liao, P., Li, W., Jiang, Y., Wu, J., Yuan, S., Fortner, J. D., & Giammar, D. E. (2017). Formation, aggregation, and deposition dynamics of non-iron colloids at anoxic-oxic interfaces. *Environmental Science and Technology*, *51*(21), 12,235–12,245. <https://doi.org/10.1021/acs.est.7b02356>

- Lovley, D. R., & Phillips, E. J. P. (1986). Organic matter mineralization with reduction of ferric iron in anaerobic sediments. *Applied and Environmental Microbiology*, 51(4), 683–689. <https://doi.org/10.1128/AEM.51.4.683-689.1986>
- Lupon, A., Denfeld, B. A., Laudon, H., Leach, J., Karlsson, J., & Sponseller, R. A. (2019). Groundwater inflows control patterns and sources of greenhouse gas emissions from streams. *Limnology and Oceanography*, 64(4), 1545–1557. <https://doi.org/10.1002/lno.11134>
- Lupon, A., Denfeld, B. A., Laudon, H., Leach, J., & Sponseller, R. A. (2020). Discrete groundwater inflows influence patterns of nitrogen uptake in a boreal headwater stream. *Freshwater Science*, 39. <https://doi.org/10.1086/708521>
- Mari, X. (1999). Carbon content and C:N ratio of transparent exopolymeric particles (TEP) produced by bubbling exudates of diatoms. *Marine Ecology Progress Series*, 183, 59–71. <https://doi.org/10.3354/meps183059>
- Marzolf, E. R., Mulholland, P. J., & Steinman, A. D. (1994). Improvements to the diurnal upstream–downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams. *Canadian Journal of Fisheries and Aquatic Sciences*, 51(7), 1591–1599. <https://doi.org/10.1139/f94-158>
- McClain, M. E., Boyer, E. W., Dent, C. L., Gergel, S. E., Grimm, N. B., Groffman, P. M., et al. (2003). Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems*, 6(4), 301–312. <https://doi.org/10.1007/s10021-003-0161-9>
- Mikutta, R., Kleber, M., Torn, M. S., & Jahn, R. (2006). Stabilization of soil organic matter: Association with minerals or chemical recalcitrance? *Biogeochemistry*, 77(1), 25–56. <https://doi.org/10.1007/s10533-005-0712-6>
- Minella, M., Marchetti, G., De Laurentiis, E., Malandrino, M., Maurino, V., Minerò, C., et al. (2014). Photo-Fenton oxidation of phenol with magnetite as iron source. *Applied Catalysis B: Environmental*, 154–155, 102–109. <https://doi.org/10.1016/j.apcatb.2014.02.006>
- Mitchell, C. P. J., & Branfireun, B. A. (2005). Hydrogeomorphic controls on reduction–oxidation conditions across boreal upland–peatland interfaces. *Ecosystems*, 8(7), 731–747. <https://doi.org/10.1007/s10021-005-1792-9>
- Morgan, B., & Lahav, O. (2007). The effect of pH on the kinetics of spontaneous Fe (II) oxidation by O₂ in aqueous solution—basic principles and a simple heuristic description. *Chemosphere*, 68(11), 2080–2084. <https://doi.org/10.1016/j.chemosphere.2007.02.015>
- Neubauer, E., Köhler, S. J., von der Kammer, F., Laudon, H., & Hofmann, T. (2013). Effect of pH and stream order on iron and arsenic speciation in boreal catchments. *Environmental Science & Technology*, 47(13), 7120–7128. <https://doi.org/10.1021/es401193j>
- Nilsson, M., Sagerfors, J., Buffam, I., Laudon, H., Eriksson, T., Grelle, A., et al. (2008). Contemporary carbon accumulation in a boreal oligotrophic minerogenic mire—A significant sink after accounting for all C-fluxes. *Global Change Biology*, 14(10), 2317–2332. <https://doi.org/10.1111/j.1365-2486.2008.01654.x>
- Paerl, H. W. (1975). Microbial attachment to particles in marine and freshwater ecosystems. *Microbial Ecology*, 2(1), 73–83. <https://doi.org/10.1007/BF02010382>
- Pan, W., Kan, J., Inamdar, S., Chen, C., & Sparks, D. (2016). Dissimilatory microbial iron reduction release DOC (dissolved organic carbon) from carbon-ferrhydrite association. *Soil Biology and Biochemistry*, 103, 232–240. <https://doi.org/10.1016/j.soilbio.2016.08.026>
- Pannard, A., Pédrone, J., Bormans, M., Briand, E., Claquin, P., & Lagadeuc, Y. (2016). Production of exopolymers (EPS) by cyanobacteria: Impact on the carbon-to-nutrient ratio of the particulate organic matter. *Aquatic Ecology*, 50(1), 29–44. <https://doi.org/10.1007/s10452-015-9550-3>
- Passow, U. (2002). Production of transparent exopolymer particles (TEP) by phyto- and bacterioplankton. *Marine Ecology-Progress Series*, 236, 1–12. <https://doi.org/10.3354/meps236001>
- Peiffer, S., Walton-Day, K., & Macalady, D. L. (1999). The interaction of natural organic matter with iron in a wetland (Tennessee Park, Colorado) receiving acid mine drainage. *Aquatic Geochemistry*, 5(2), 207–223. <https://doi.org/10.1023/A:1009617925959>
- Peter, S., Isidorova, A., & Sobek, S. (2016). Enhanced carbon loss from anoxic lake sediment through diffusion of dissolved organic carbon. *Journal of Geophysical Research: Biogeosciences*, 121, 1959–1977. <https://doi.org/10.1002/2016JG003425>
- Poulin, B. A., Ryan, J. N., & Aiken, G. R. (2014). Effects of iron on optical properties of dissolved organic matter. *Environmental Science & Technology*, 48(17), 10,098–10,106. <https://doi.org/10.1021/es502670r>
- Quigg, A., Passow, U., Chin, W.-C., Xu, C., Doyle, S., Bretherton, L., et al. (2016). The role of microbial exopolymers in determining the fate of oil and chemical dispersants in the ocean. *Limnology and Oceanography Letters*, 1(1), 3–26. <https://doi.org/10.1002/lol2.10030>
- Raymond, P. A., Saiers, J. E., & Sobczak, W. V. (2016). Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. *Ecology*, 97(1), 5–16. <https://doi.org/10.1890/14-1684.1>
- Reuter, H., Gensel, J., Elvert, M., & Zak, D. (2020). Evidence for preferential protein depolymerization in wetland soils in response to external nitrogen availability provided by a novel FTIR routine. *Biogeosciences*, 17, 499–514. <https://doi.org/10.5194/bg-17-499-2020>
- Riedel, T., Zak, D., Biester, H., & Dittmar, T. (2013). Iron traps terrestrially derived dissolved organic matter at redox interfaces. *Proceedings of the National Academy of Sciences*, 110(25), 10,101–10,105. <https://doi.org/10.1073/pnas.1221487110>
- Rydin, H., & Jørgensen, J. K. (2013). *The biology of peatlands* (2nd ed.). Oxford: Oxford University Press.
- Scheel, T., Haumaier, L., Ellerbrock, R. H., Rühlmann, J., & Kalbitz, K. (2008). Properties of organic matter precipitated from acidic forest soil solutions. *Organic Geochemistry*, 39(10), 1439–1453. <https://doi.org/10.1016/j.orggeochem.2008.06.007>
- Seekell, D. A., Lapierre, J.-F., Ask, J., Bergström, A.-K., Deininger, A., Rodríguez, P., & Karlsson, J. (2015). The influence of dissolved organic carbon on primary production in northern lakes: Influence of DOC on production. *Limnology and Oceanography*, 60(4), 1276–1285. <https://doi.org/10.1002/lno.10096>
- Sheng, G.-P., Zhang, M.-L., & Yu, H.-Q. (2008). Characterization of adsorption properties of extracellular polymeric substances (EPS) extracted from sludge. *Colloids and Surfaces B: Biointerfaces*, 62(1), 83–90. <https://doi.org/10.1016/j.colsurfb.2007.09.024>
- Simon, M., Grossart, H.-P., Schweitzer, B., & Ploug, H. (2002). Microbial ecology of organic aggregates in aquatic ecosystems. *Aquatic Microbial Ecology*, 28(2), 175–211. <https://doi.org/10.3354/ame028175>
- Sodano, M., Lerda, C., Nisticò, R., Martin, M., Magnacca, G., Celi, L., & Said-Pullicino, D. (2017). Dissolved organic carbon retention by coprecipitation during the oxidation of ferrous iron. *Geoderma*, 307, 19–29. <https://doi.org/10.1016/j.geoderma.2017.07.022>
- Sollins, P., Homann, P., & Caldwell, B. A. (1996). Stabilization and destabilization of soil organic matter: Mechanisms and controls. *Geoderma*, 74(1–2), 65–105. [https://doi.org/10.1016/S0016-7061\(96\)00036-5](https://doi.org/10.1016/S0016-7061(96)00036-5)
- Starkey, J. E., & Karr, P. R. (1984). Effect of low dissolved oxygen concentration on effluent turbidity. *Journal—Water Pollution Control Federation*, 56(7), 837–843. Retrieved from <https://www.jstor.org/stable/25042360>
- Stephens, M. B. (2009). *Synthesis of the bedrock geology in the Bergslagen region, Fennoscandian Shield, south-central Sweden, Sveriges geologiska undersökning. Serie Ba, Översiktskartor med beskrivningar* (Vol. 58, pp. 1–259). Uppsala, Sweden: Sveriges geologiska undersökning (SGU).
- Tank, S. E., Fellman, J. B., Hood, E., & Kritzbeg, E. S. (2018). Beyond respiration: Controls on lateral carbon fluxes across the terrestrial-aquatic interface. *Limnology and Oceanography Letters*, 3(3), 76–88. <https://doi.org/10.1002/lol2.10065>

- Tisdall, J. M. (1994). Possible role of soil microorganisms in aggregation in soils. *Plant and Soil*, *159*(1), 115–121. <https://doi.org/10.1007/BF00000100>
- Torgersen, T., & Branco, B. (2008). Carbon and oxygen fluxes from a small pond to the atmosphere: Temporal variability and the CO₂/O₂ imbalance: Carbon fluxes from a small pond. *Water Resources Research*, *44*, W02417. <https://doi.org/10.1029/2006WR005634>
- Tranvik, L. J., & Sieburth, J. M. N. (1989). Effects of flocculated humic matter on free and attached pelagic microorganisms. *Limnology and Oceanography*, *34*(4), 688–699. <https://doi.org/10.4319/lo.1989.34.4.0688>
- Vähätalo, A. V., Aarnos, H., & Mäntyniemi, S. (2010). Biodegradability continuum and biodegradation kinetics of natural organic matter described by the beta distribution. *Biogeochemistry*, *100*(1), 227–240. <https://doi.org/10.1007/s10533-010-9419-4>
- Vermeer, A. W. P., van Riemsdijk, W. H., & Koopal, L. K. (1998). Adsorption of humic acid to mineral particles. 1. Specific and electrostatic interactions. *Langmuir*, *14*(10), 2810–2819. <https://doi.org/10.1021/la970624r>
- Viollier, E., Inglett, P. W., Hunter, K., Roychoudhury, A. N., & Van Cappellen, P. (2000). The ferrozine method revisited: Fe (II)/Fe (III) determination in natural waters. *Applied Geochemistry*, *15*(6), 785–790. [https://doi.org/10.1016/s0883-2927\(99\)00097-9](https://doi.org/10.1016/s0883-2927(99)00097-9)
- von Wachenfeldt, E., Bastviken, D., & Tranvika, L. J. (2009). Microbially induced flocculation of allochthonous dissolved organic carbon in lakes. *Limnology and Oceanography*, *54*(5), 1811–1818. <https://doi.org/10.4319/lo.2009.54.5.1811>
- Wallace, J. B., Whiles, M. R., Eggert, S., Cuffney, T. F., Lugthart, G. J., & Chung, K. (1995). Long-term dynamics of coarse particulate organic matter in three Appalachian Mountain streams. *Journal of the North American Benthological Society*, *14*(2), 217–232. <https://doi.org/10.2307/1467775>
- Wang, H., River, M., & Richardson, C. J. (2019). Does an 'iron gate' carbon preservation mechanism exist in organic-rich wetlands? *Soil Biology and Biochemistry*, *135*, 48–50. <https://doi.org/10.1016/j.soilbio.2019.04.011>
- Ward, N. D., Sawakuchi, H. O., Neu, V., Less, D. F. S., Valerio, A. M., Cunha, A. C., et al. (2018). Velocity-amplified microbial respiration rates in the lower Amazon River. *Limnology and Oceanography Letters*, *3*(3), 265–274. <https://doi.org/10.1002/lol2.10062>
- Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology*, *37*(20), 4702–4708. <https://doi.org/10.1021/es030360x>
- Wingender, J., Neu, T. R., & Flemming, H.-C. (2012). *Microbial extracellular polymeric substances: Characterization, structure and function*. Berlin: Springer Science & Business Media.
- Wotton, R. S. (1994). *The Biology of Particles in Aquatic Systems* (2nd ed., pp. 1–336). Boca Raton, FL: Lewis Publishers, CRC Press.
- Xu, C., Zhang, S., Chuang, C., Miller, E. J., Schwehr, K. A., & Santschi, P. H. (2011). Chemical composition and relative hydrophobicity of microbial exopolymeric substances (EPS) isolated by anion exchange chromatography and their actinide-binding affinities. *Marine Chemistry*, *126*(1), 27–36. <https://doi.org/10.1016/j.marchem.2011.03.004>
- Zak, D., Gelbrecht, J., & Steinberg, C. E. W. (2004). Phosphorus retention at the redox interface of peatlands adjacent to surface waters in northeast Germany. *Biogeochemistry*, *70*(3), 357–368. <https://doi.org/10.1007/s10533-003-0895-7>
- Zhou, C., Liu, Y., Liu, C., Liu, Y., & Tfaily, M. M. (2019). Compositional changes of dissolved organic carbon during its dynamic desorption from hyporheic zone sediments. *Science of the Total Environment*, *658*, 16–23. <https://doi.org/10.1016/j.scitotenv.2018.12.189>