

# This is a self-archived version of an original article. This version may differ from the original in pagination and typographic details.

Author(s): Riise, Gunnhild; Haaland, Ståle Leif; Xiao, Yihua

Title: Coupling of iron and dissolved organic matter in lakes–selective retention of different size fractions

Year: 2023

Version: Published version

Copyright: © The Author(s) 2023

Rights: In Copyright

Rights url: http://rightsstatements.org/page/InC/1.0/?language=en

# Please cite the original version:

Riise, G., Haaland, S. L., & Xiao, Y. (2023). Coupling of iron and dissolved organic matter in lakes–selective retention of different size fractions. Aquatic Sciences, 85(2), Article 57. https://doi.org/10.1007/s00027-023-00956-w **RESEARCH ARTICLE** 

# Aquatic Sciences



# Coupling of iron and dissolved organic matter in lakes–selective retention of different size fractions

Gunnhild Riise<sup>1</sup> · Ståle Leif Haaland<sup>1</sup> · Yihua Xiao<sup>1,2,3</sup>

Received: 1 September 2022 / Accepted: 11 March 2023 © The Author(s) 2023

#### Abstract

Increasing concentration of iron (Fe) is observed in many boreal lakes, such as for the present study in Oslo Østmark, SE-Norway (1983–2018). As Fe-regulating processes are complex and dynamic, the link between mobilizing and retention processes is still not well understood. A seasonal study (2017–2018) from two headwaters, with medium and high dissolved organic matter (DOM) concentrations, showed that the loading of Fe to the lakes was highly dependent on flow conditions. Significantly higher values of Fe were related to autumn and winter periods with high runoff of highly colored and aromatic DOM compared to a severe drought period with minimum Fe values in the lakes. Compared to DOM, a significantly larger part of Fe was in a colloidal form, and a size-selective process (dependent on flow and water retention time) seemed to preferentially settle Fe compared to DOM. In contrast to Fe, the variability in DOM concentrations was moderate through the whole year. However, there were significant changes in the spectroscopic properties of DOM, with decreased fluorescence intensity and increased spectral slope during the warm dry season, indicating increased importance of DOM turnover in the lake. As Fe was transported from the catchment during high flow condition, at the same time as the oxic form of sulfur (SO<sub>4</sub><sup>2-</sup>), there was no sign of retention of Fe as FeS. We conclude that the mobilization and retention of compounds that are mainly in a colloidal form, such as Fe, are especially vulnerable to changes in flow conditions, suggesting increased variation in Fe levels in a future climate with increased frequency of flooding and drought episodes.

Keywords Iron · Dissolved organic matter · Mobilization · Retention · Colloidal fraction · Sulfate

# Introduction

Despite low water solubility, iron (Fe), as a common component of the Earth's crust (5%), plays an important role in the biogeochemical cycling of nutrients (C, N and P) and trace metals (Temnerud et al. 2013). Enhanced values of Fe in waters impact the aquatic biota, both directly (Heikkinen et al. 2022; Vuori 1995) and indirectly through the browning of freshwaters (Xiao and Riise 2021) by changing the light (Kritzberg et al. 2020) and temperature regime (Read and

⊠ Yihua Xiao yihua.xiao@qut.edu.cn

- <sup>1</sup> Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, 1432 Ås, Norway
- <sup>2</sup> School of Environmental and Municipal Engineering, Qingdao University of Technology, Qingdao 266033, China
- <sup>3</sup> Department of Biological and Environmental Science, University of Jyväskylä, 40014 Jyväskylä, Finland

Rose 2013). Knowledge on factors that regulate the coupling of Fe between the terrestrial and aquatic phase are, therefore, essential for understanding the function of several ecosystem processes.

Recently, Fe concentrations have increased in several boreal lakes, especially in Northern Europe (Björnerås et al. 2017; Kritzberg and Ekström 2012; Weyhenmeyer et al. 2014). Key factors that regulate the mobility and retention of Fe in the aquatic environment are pH, organic matter (OM) and redox conditions (Björnerås et al. 2019; Neubauer et al. 2013). As has long been known, interaction of Fe with organic colloids provides enhanced levels of Fe in humic waters (Ruttner 1953), and recent studies verified that Fe dissolved organic matter complexes (Fe-DOM) promote increased transport of Fe (Herzog et al. 2020). Along with increased runoff of OM, several areas have, therefore, experienced increased transport of Fe from the terrestrial catchment during the acid rain recovery period (Björnerås et al. 2017). Apart from being a mobilizing factor for OM, and thereby Fe-organic complexes, reduced deposition of sulfate (SO<sub>4</sub><sup>2-</sup>) might also impact the cycling of Fe in other ways. The rate of microbial reduction of SO<sub>4</sub><sup>2-</sup> might be limited by the amount of SO<sub>4</sub><sup>2-</sup> (Feng and Hsieh 1998), potentially impacting the formation of non-mobile FeS/ FeS<sub>2</sub> (Raiswell and Canfield 2012). Reduced acid deposition of sulfur (S) might therefore be a mobilizing factor for Fe through less formation of FeS/FeS<sub>2</sub>. A contrasting view on this matter has, however, been put forward, as reduced S deposition was not found to be a driver behind increasing Fe concentration as rather reducing conditions, climate-related factors like higher temperature and moisture and expansion of coniferous forests were more important (Björnerås et al. 2019, 2022).

The link between the terrestrial and aquatic environment is dependent on runoff conditions, which impact both the hydrological connectivity and redox states in the catchment. High flow conditions may promote increased runoff of Fe (Xiao and Riise 2021) where especially high-molecularweight (H-Mw) Fe-DOM compounds (Riise et al. 1994) from shallow organic layers are mobilized (Laudon et al. 2011). In addition, the land-water interfaces (e.g., riparian zones), the gradient where there is a change from anoxic to oxic conditions (oxyline), is of major importance for the fate of Fe (Lidman et al. 2017). Here, Fe is assumed to be retained by precipitation to Fe(oxy)hydroxides in the transition from the anoxic to oxic zone. Changes in the groundwater table have a substantial impact on Fe fractions and their mobility (Ingri et al. 2018). Enhanced water saturation may result in more anoxic water with a high concentration of soluble Fe(II) that feeds into surface waters (Kritzberg and Ekström 2012).

Although Fe-DOM complexes are relatively stable (Herzog et al. 2020), the concentration of Fe significantly declines with increasing retention time along the aquatic continuum (Weyhenmeyer et al. 2014). Fe-(oxy)hydroxides are more prone to aggregation than Fe-OM complexes (Herzog et al. 2020), and there is a preferential loss of Fe in relation to color and OM in lake sediments (Björnerås et al. 2021). Also, Köhler et al. (2013) have found a shorter halflife for Fe than colored DOM and DOC in one of the larger lakes of Sweden (Köhler et al. 2013). Thus, although DOM keeps Fe in solution, in-lake processes contribute to a selective retention of Fe compared to DOM. Fe-DOM complexes are, however, also found in aggregates, suggesting that not only the respective phases alone, but also factors such as colloidal size and chemical composition of DOM may impact the behavior of Fe species (Herzog et al. 2017).

Fe-regulating processes are very dynamic and vary in space and time, where extreme weather conditions are supposed to increase the variability even more (Xiao and Riise 2021). Knowledge is still needed to understand processes regulating the cycling of Fe, with important questions related to (1) long-term and seasonal changes in Fe-DOM complexes in relation to lake browning and (2) size-selective retention of Fe-DOM complexes in lakes in relation to flow conditions.

Headwater lakes are directly coupled to their surrounding catchment and respond quickly to changes in the terrestrial input of Fe without being influenced by downstream processes. In a boreal lake district of Østmarka, Norway, long-term trends and seasonal variability in Fe are studied in two headwater lakes. Here, size fractionated water samples have been optically characterized to gain insight into Fe-organic complexes and seasonal processes regulating the retention and mobility of Fe. In this study, we hypothesize that seasonal and annual variability in flow impact (1) the hydrological connectivity and the transfer of Fe-DOM to the lake and, (2) the size-selective removal of different Fe fractions in lakes.

# **Field sites and methods**

#### Water samples and catchment characteristics

Long-term study: Water samples were collected from Lake Langvann and Lake Solbergvann (Fig. 1) in the boreal lake district of Oslo Østmark (59°50'N, 11°00'E) during the autumn circulation period (from late October to early November) at 0.5 m depth in 1983, 1996, 1997, 2000, 2001, 2004, 2005 and then annually from 2007 to 2018 (19 sampling years, Fig. S1). Seasonal study: In addition, Lake Langvann and Lake Solbergvann were subjected to a study from November 2017 to October 2018, in total eight times. Lake Langvann and Lake Solbergvann are low ionic headwater lakes, with catchment areas of 0.871 and 0.131 km<sup>2</sup>, respectively (Fig. 1). Estimated water retention times are approximately 1 year for Lake Langvann and 0.5 year for Lake Solbergvann, where annual runoff is  $18.5 \text{ L} (\text{s km}^2)^{-1}$ for both catchments (data were extracted from Norwegian Water Resources and Energy Directorate NVE and Precipitation Field-Water Flow-Index-Analysis, NEVINA). The catchments are mostly covered by coniferous forest (Lake Langvann 79% and Lake Solbergvann 90%), and open lake areas cover 12.6% of Lake Langvann and 9.5% of Lake Solbergvann. In addition, Lake Langvann is also surrounded by some peatland (8.3%). According to quaternary maps, the catchment of Lake Solbergvann is covered by a thin humic peat cover, while the catchment of Lake Langvann is partly covered by thin moraine, giving rise to somewhat thicker soil cover in the northern part of its catchment (data were extracted from the website of Geological Survey of Norway). The small size and elongated shape of Lake Solbergvann suggest that large parts of the lake water have close contact with the terrestrial catchment area (Fig. 1).



Fig. 1 Catchment area and locations of Lake Solbergvann (upper right) and Lake Langvann (lower right) in Oslo Østmark (59°50'N, 11°00'E), Southeast Norway

Lake Langvann has medium values for total organic carbon (TOC, 5.8 mg L<sup>-1</sup>) and color (40 Pt mg L<sup>-1</sup>), while Lake Solbergvann is characterized as a humic lake with high values for TOC (14.4 mg L<sup>-1</sup>) and color (138 Pt mg L<sup>-1</sup>) (Table 1). Proxies for the aromaticity and molecular weight (color/TOC ratio and SUVA<sub>254</sub>) of DOM show higher values for the humic lake compared to the medium-humic lake. Also, the Fe concentration is higher for Lake Solbergvann compared to Lake Langvann because of more extensive complexation of Fe with DOM in the humic lake. Average pH values and SO<sub>4</sub><sup>2-</sup> show similar levels for the two lakes, while the conductivity and Ca cation concentrations are higher for Lake Solbergvann. It must be noted that numbers given in Table 1 are average values over a long time period, where changes in weather conditions and acid rain deposition have resulted in great variability among years and along a yearly timeline.

#### Climate

Long-term changes: Long-term (1961–1990) annual mean precipitation and annual temperature, at a close meteorological station (Oslo-Blindern), are 763 mm year<sup>-1</sup> and 5.7 °C. Annual deviations from this "normal period" are shown in Fig. S1. Especially, there have been increased levels of precipitation since 2000. For temperature, there have generally been higher annual values since 1988, with only 2 years showing lower annual temperature than normal.

Table 1 Mean ± standard deviation (SD) and range for Fe-related variables during the autumn circulation period from 1983 to 2018 for Lake Langvann and Lake Solbergvann in the Østmarka lake district of Norway (n = 19)

	Langvann		Solbergvann	
	Mean (±SD)	Range	Mean (±SD)	Range
$\overline{\text{Fe}(\text{mg }\text{L}^{-1})}$	0.199 (±0.101)	0.060-0.460	0.291 (±0.069)	0.180-0.440
TOC (mg $L^{-1}$ )	$5.8 (\pm 0.9)$	4.0-8.1	$14.4 (\pm 2.0)$	10.0-16.9
Color (Pt mg $L^{-1}$ )	40 (±15)	10-80	138 (±38)	60-202
Fe/TOC ratio	$0.03 (\pm 0.02)$	0.01-0.08	$0.020(\pm 0.003)$	0.015-0.027
Color/TOC ratio	6.7 (±1.9)	2.0-9.9	9.5 (±1.9)	4.9-12.8
$SUVA_{254}^{*} (L \text{ mg } C^{-1} \text{ m}^{-1})$	$9.0(\pm 0.9)$	6.8-10.1	10.9 (±1.2)	9.2-13.5
pH	5.9 (±0.4)	5.0-6.7	5.9 (±0.3)	5.2-6.3
Cond. ( $\mu$ S cm <sup>-1</sup> )	23.6 (±3.0)	21.0-31.0	32.8 (±5.0)	27.9-45.0
$SO_4^{2-}$ (mg L <sup>-1</sup> )	3.3 (±1.3)	2.3-7.6	$3.3(\pm 1.5)$	2.2-8.5
$Cl^{-}$ (mg $L^{-1}$ )	$2.3 (\pm 0.3)$	1.6-2.9	$2.6(\pm 0.5)$	1.9-3.6
$Ca (mg L^{-1})$	$1.5 (\pm 0.2)$	1.3-2.0	$3.2(\pm 0.5)$	2.4-4.5

\*SUVA<sub>254</sub> = specific UV absorption at 254 nm ( $a_{254}$ /TOC ratio, L mg C<sup>-1</sup> m<sup>-1</sup>); Cond. = conductivity

Seasonal variations: The monthly precipitation during the period from November 2017 to October 2018 showed higher values than normal for January and September, while the period from March to September was exceptionally dry (Fig. 2). In July, the monthly precipitation was only 16 mm compared to a "normal" precipitation of 87 mm. February and March were colder, while May through July was warmer than the normal period. July 2018 had an average temperature of 22.2 °C compared to a "normal" value of 17.7 °C.

#### Laboratory analyses

Water samples were transported to the soil and water laboratory, Norwegian University of Life Sciences (NMBU in Ås, Norway), for analyses of Fe, TOC, color, Fe, pH, conductivity,  $SO_4^{2-}$ , Cl<sup>-</sup> and other chemical variables (Table 1).

Absorbance at wavelength 410 nm  $(a_{410})$  of 0.45-µm filtered water samples was measured according to the national standard method (Norwegian Standard Association 2002) and then converted to water color units of Pt mg  $l^{-1}$ (Hongve and Åkesson 1996). The absorption coefficients for 410 nm and 254 nm were obtained by the function of  $a_{(\lambda)} = 2.303 A_{(\lambda)}/L$ , where  $A_{(\lambda)}$  is the measured absorbance at wavelength, and  $\lambda$  (nm) and L (m) are the length of the light path.

The UV-Vis spectra (200-700 nm) of 0.45-µm filtered water samples were measured using a Hitachi spectrophotometer (UH5300, Hitachi). The spectral slope coefficient was obtained by linear regression, calculated from the lntransformed absorption coefficient using the wavelength range of 275 to 295 nm ( $S_{275-295}$ ,  $\mu m^{-1}$ ) (Helms et al. 2008). The carbon-normalized absorption (SUVA<sub>254</sub>, specific UV absorption at 254 nm with a unit of L mg  $C^{-1}$  m<sup>-1</sup>) was calculated by dividing the absorption coefficient  $(a_{254})$  by DOC concentration (Weishaar et al. 2003). The indices  $S_{275-295}$ 



Fig. 2 Monthly precipitation (mm) and monthly average temperature (°C) in the period from November 2017 to October 2018 compared to normal values (1971-1990)

and SUVA<sub>254</sub> are calculated as proxies of DOM molecular weight and aromaticity, respectively (Helms et al. 2008; Kida et al. 2018; Li et al. 2017).

TOC was measured by a Shimadzu TOC 5000 carbon analyzer based on high temperature combustion. Due to low content of nutrients and time of sampling (late autumn), the primary productivity in the long-term study was low (Riise et al. 2018). In addition, turbidity measurements have proven that the particle content is very low. Therefore, as for many boreal lakes, there were no significant differences between DOC and TOC (Hongve et al. 2004; Mattsson et al. 2005). The total concentrations of Fe and calcium were measured by a Perkin-Elmer atomic absorption spectrometer (Model 460) in 1983 and for the following years by inductively coupled plasma mass spectrometry (ICP-MS, Agilent). Other chemical variables were analyzed according to the national standards found in Hongve et al. (2004).

Fluorescent excitation-emission matrices (EEMs) of 0.45-µm filtered water samples were measured using a Cary Eclipse Fluorescence Spectrophotometer (Varian). The excitation wavelength (Ex) range was from 240 to 450 nm and emission wavelength (Em) range from 300 to 600 nm. The intervals for Ex and Em were 5 nm and 2 nm, respectively. The slit width for both Ex and Em was 5 nm. A blank EEM (Milli-Q, Millipore) with identical setting was scanned each day before the measurements of water samples.

A total of 32 fluorescent EEMs were collected and analyzed by parallel factor modeling (PARAFAC). The PARA-FAC modeling was conducted using the DOMFluor toolbox following the protocol described by Stedmon and Bro (2008). In the modeling, spectral correction, background subtraction, inner filter effect correction and Raman normalization were conducted (Murphy et al. 2013). A non-negativity constraint was applied, and the number of the components was validated by split-half validation. The PARAFAC modeling was carried out with MATLAB R2020b software (Mathworks, USA). The maximum fluorescent intensities in Raman unit (RU) of identified components were reported.

## Size fractionation

All samples from the seasonal study were fractionated by molecular size with a centrifugal filter device (nominal molecular weight cutoff 10 kDa, Centriprep<sup>®</sup> from Amicon and Merck Millipore) at  $3000 \times g$  for 20 min. Prior to use, the centrifugal filter device was washed with 0.01 mol L<sup>-1</sup> NaOH and 0.01 mol L<sup>-1</sup> HNO<sub>3</sub> and then rinsed with Milli-Q (Millipore) three times. The ultrafiltrates (<10 kDa) were analyzed for organic carbon, Fe and fluorescence using the same method as mentioned above.

## Statistical analysis

Trends in lake water quality for the long-term study (1983–2018) were determined based on a non-parametric Mann-Kendall trend analysis (Salmi et al. 2002). Sigmaplot

14 was used for statistical comparison of differences between the two lakes (t-tests) and individual differences in the separate lakes concerning size fractionations (one-way analysis of variance). Principal component analysis (PCA) was conducted in Rstudio 3.5.1 (2019–2018 Rstudio, Inc.) with "stats" package. The significance levels were set at P < 0.001, P < 0.01, P < 0.05 and P < 0.1.

# Results

### Long-term trends

Both lakes showed a significant reduction in  $SO_4^{2-}$ , Ca and conductivity during the acid rain recovery period, while pH showed no significant change for Lake Langvann and a small reduction for Lake Solbergvann (Table 2). Although the recent Fe, TOC and color values were generally higher compared to earlier times for both lakes, only Lake Solbergvann showed a significant monotonic trend for these color-related variables (Table 2). The long-term trends for Fe, TOC and color in Lake Langvann were not significant. The color contribution from Fe was higher for Lake Langvann (11.0%) than for the humic Lake Solbergvann (5.0%) (Xiao and Riise 2021). The Fe/TOC ratio increased in Lake Langvann, indicating an increased color contribution from Fe with time, while for Lake Solbergvann the color/TOC ratio increased with time, i.e., the color absorption of DOM increased (Table 2).

**Table 2** Annual trend analysis (Mann-Kendall) for Lake Langvann (n = 19) and Lake Solbergvann (n = 19). Data from 1983 to 2018 were used

	Lake Langvann Mann-Kendall trend		Lake Solbergvann Mann-Kendall trend	
	Test Z	Significance	Test Z	Significance
Fe (mg $L^{-1}$ )	1.47		3.55	***
TOC (mg $L^{-1}$ )	1.54		3.85	***
Color (Pt mg $L^{-1}$ )	1.33		3.19	**
Fe/TOC ratio	1.72	+	1.47	
Color/TOC ratio	0.84		1.96	+
SUVA <sub>254</sub>	-0.03		0.00	
рН	0.07		-2.42	*
Cond. ( $\mu$ S cm <sup>-1</sup> )	-2.62	**	-3.34	***
$SO_4^{2-}$ (mg L <sup>-1</sup> )	-4.80	***	- 3.99	***
$Cl^{-}(mg L^{-1})$	-1.68	+	-2.14	*
Ca (mg L <sup>-1</sup> )	-2.78	**	-2.95	**

Cond. = conductivity

\*\*\*If trend at  $\alpha = 0.001$  level of significance, \*\* if trend at  $\alpha = 0.01$  level of significance, \* if trend at  $\alpha = 0.05$  level of significance, + if trend at  $\alpha = 0.1$  level of significance (Salmi et al. 2002)

## **Seasonal variations**

There were significant declines in the Fe concentrations during the summer drought, with minimum concentrations of 47 µg  $L^{-1}$  and 83 µg  $L^{-1}$  for Lake Langvann and Lake Solbergvann in July 2018. Maximum values of Fe appeared in May and November, with values of 227 µg  $L^{-1}$  and 360 µg  $L^{-1}$  for Lake Langvann and Lake Solbergvann, respectively.

The precipitation-related water soluble anions Cl<sup>-</sup> and  $SO_4^{2-}$  showed similar trends for both lakes during the period from November 2017 to November 2018 (Fig. 3). However, seasonal separation of these two ions occurred during the summer drought period. While Cl<sup>-</sup> showed small variations with time,  $SO_4^{2-}$  showed a significant reduction in concentration during the summer drought. Especially for Lake Langvann, the  $SO_4^{2-}$  decrease was extensive, as the concentration decreased from 2.4 mg L<sup>-1</sup> to 0.4 mg L<sup>-1</sup> in the period from 10 June to 27 July 2018 before it attained similar values as in spring. The highest seasonal pH values also

coincided with the summer period with lowest  $SO_4^{2-}$  values for both lakes (Fig. 3).

#### **Fractionation analyses**

The main part of Fe belonged to the high H-Mw fraction, which also can be categorized as the colloidal fraction (0.45  $\mu$ m–10 kDa). For Lake Langvann and Lake Solbergvann, average percentage values for colloidal Fe for the whole season were  $84 \pm 5\%$  and  $64 \pm 8\%$ , respectively (Fig. 4). In contrast, for TOC the major part belonged to the Low molecular weight (L-Mw) fraction (<10 kDa), although colloidal OM was significantly higher (Table S1) for the humic Lake Solbergvann ( $27 \pm 5\%$ ) compared to medium-humic Lake Langvann ( $13 \pm 6\%$ ). Thus, colloidal Fe was significantly higher and colloidal OM significantly lower for Lake Langvann compared to Lake Solbergvann, respectively (Table S1). Concerning the absorption characteristics, approximately 50% of the color ( $a_{410}$ ) and between



Fig. 3 Seasonal variations in Fe ( $\mu$ g L<sup>-1</sup>), SO<sub>4</sub><sup>2-</sup> (mg L<sup>-1</sup>), Cl<sup>-</sup> (mg L<sup>-1</sup>) and TOC (mg L<sup>-1</sup>) for Lake Langvann and Solbergvann for the period from November 2017 to November 2018

30 and 40% of the UV absorption ( $a_{254}$ ) were related to the colloidal fraction for the whole season on average. In contrast, for fluorescence, the major part was related to L-Mw compounds (<10 kDa), where 85%–96% and 76%–98% of total fluorescence belonged to the L-Mw fraction for Lake Langvann and Solbergvann, respectively (Fig. 4). Thus, there were significant variations in the distribution among size fractions for Fe, TOC and the absorption and fluorescence characteristics in both lakes (Table S2).

## Spectral characteristics of DOM

#### **UV** absorption

The spectral slope  $S_{275-295}$  showed similar trends during the season for both lakes. Relatively low values of  $S_{275-295}$ (13.6–14.2 µm<sup>-1</sup> for Lake Langvann and 12.8–13.2 µm<sup>-1</sup> for Lake Solbergvann) were found for the period from November 2017 to May 2018 (Fig. 5). Then, there was a sharp increase in the spectral slope  $S_{275-295}$  during the summer drought from June to July 2018 for both lakes. After the summer drought, the  $S_{275-295}$  values decreased from 16.7 µm<sup>-1</sup> (July 2018) to 15.1 µm<sup>-1</sup> (October 2018) and from 14.1 µm<sup>-1</sup> (July 2018) to 13.2 µm<sup>-1</sup> (October 2018) for Lake Langvann and Lake Solbergvann, respectively (Fig. 5).

The specific UV absorption, SUVA<sub>254</sub> for the mediumhumic lake was significantly lower (P < 0.001) compared to the humic lake (Fig. 5). In Lake Langvann, there was an obvious increase in the SUVA<sub>254</sub> value in May, which decreased sharply in July 2018 (Fig. 5). Compared to Lake Langvann, the SUVA<sub>254</sub> values for Lake Solbergvann were much more stable with smaller variations.

#### **Fluorescence intensity**

A total of three fluorescent components (C1, C2 and C3) were identified by EEMs-PARAFAC modeling. According to previous studies, fluorescent components C1 (Ex: 360(290) nm; Em: 474 nm) and C2 (Ex: 260 nm; Em: 460 nm) can be categorized as allochthonous terrestrial-derived humic-like substances that are resistant to microbial degradation (Jørgensen et al. 2011; Stedmon and Markager 2005), while the fluorescent component C3 (Ex: 335 nm; Em: 420 nm) is categorized as autochthonous humic-like substances derived from microbial activities or by-products of photodegradation of organic compounds (Helms et al. 2013, 2014; Kothawala et al. 2014).

The total fluorescent intensity was higher in the humic Lake Solbergvann (0.59–3.8 RU) than in the medium-humic lake Langvann (1.2–9.8 RU, Fig. 4). Although the concentrations of TOC did not show significant seasonal variations in either of the lakes, we observed remarkably seasonal reductions in fluorescence intensity of DOM for both lakes (Figs. 4, 5). Peaking values of fluorescent intensities were found in November 2017 and January 2018 for both lakes (Fig. 5) while the contribution of the autochthonous fraction was low (Fig. 5). After January 2018, there were severe reductions in fluorescence intensities for both lakes (Fig. 4). The seasonal trends for the allochthonous and autochthonous derived fractions of OM were rather similar in Lake Langvann and Lake Solbervann (Fig. 5).

PCA analysis of key variables for possible importance for regulation of Fe showed that the PC1 axis explained 51.2% and PC2 19.7% of the variability (Fig. 6). According to the PCA plot, the variability in Fe can first be explained by spectroscopic properties of DOM with a positive relation between Fe and the fluorescence characteristics and a negative relationship to the spectral slope of DOM ( $S_{275-295}$ ), as also shown in Fig. 5. SUVA<sub>254</sub> was directly related to TOC, indicating a change in spectroscopic properties of organic matter with increasing concentration of TOC. Although the arrows were pointing in the same direction, there was a direct correlation between neither TOC and Fe nor Fe and accumulated precipitation. The drought episode can clearly be visualized from Fig. 6 as temperature and precipitation are inversely related. During the dry and warm period, higher primary production contributed to rising pH values and lack of water to a preferential retention of  $SO_4^{2-}$ .

# Discussion

# Long-term trends in Fe – differences between the two lakes

During the acid rain recovery period, the annual declines in  $SO_4^{2-}$  for the two lakes were significant and followed each other closely (Table 2). This result indicates a similar response to reduced deposition of  $SO_4^{2-}$  and small differences in storage/retention and mobility of  $SO_4^{2-}$  between these two catchments. Concurrent with the reduction in  $SO_4^{2-}$ , there were significant reductions in Ca cations and conductivity for both lakes. Higher Ca levels in the humic lake (Lake Solbergvann) compared to the medium-humic lake (Lake Langvann) were probably neutralized by high concentrations of organic anions in the humic lake.

For the humic Lake Solbergvann, there was a significant increase in TOC, color and Fe as opposed to the mediumhumic Lake Langvann (Table 2). The thin peaty humic layer of the catchment of Lake Solbergvann apparently caused the higher loading of DOM compared to Lake Langvann, where the soil cover is somewhat more extensive. Unlike Lake Solbergvann, the Fe/TOC ratio has been increasing for Lake Langvann, suggesting an increased runoff of Fe minerals compared to OM, in line with a significantly higher proportion of Fe colloids for Lake Langvann compared to



**<**Fig. 4 Fe ( $\mu$ g L<sup>-1</sup>) in the first row,  $a_{410}$  (m<sup>-1</sup>) in the second row,  $a_{254}$  (m<sup>-1</sup>) in the third row, TOC (mg L<sup>-1</sup>) in the fourth row and fluorescence intensity (RU) in the fifth row in size fractionated lake water samples (L-Mw>10 kDa and H-Mw>10 kDa) during the period from November 2017 to November 2018

Lake Solbergvann (Table S1). Lake Solbergvann, however, has a higher proportion of colloidal DOM (Fig. 4), which likely has a less mobile and more aromatic character (high  $SUVA_{254}$ , Fig. 5), indicating shorter transport distance and lower impact from in-lake processes than for Lake Langvann. This result agrees with a shorter water retention time for Lake Solbergvann compared to lake Langvann. The importance of water residence time for DOM properties was previously stressed by Köhler et al. (2013).

Lake Langvann showed large annual variability for TOC, color and Fe, where extensive concentration peaks and troughs for different years did not support long monotonic term trends (Table 2). Thus, Lake Langvann seems to be more susceptible to annual changes in hydrologically related factors (e.g., runoff, water retention time) that cause strong seasonal and annual shifts in DOM properties.

## **Seasonal variations**

The concentration of Fe showed large seasonal variability compared to TOC during the period from November 2017 to November 2018 (Fig. 3). The lowest Fe concentration was found in July 2018 in both lakes when the monthly precipitation and catchment loading of Fe probably were at their lowest (Fig. 2). An increase in temperature and pH and a higher autochthonous proportion of the fluorescent fraction C3 support the enhanced importance of primary production and in-lake processes (Figs. 2, 3, 5). Although Fe decreased in concentration during the summer drought, the colloidal fraction of Fe was clearly dominating the whole year through (Fig. 4). Since colloidal Fe is susceptible to time-dependent aggregation and settling processes (Xiao and Riise 2021), and Fe is found to decrease with decreasing retention time in the landscape (Weyhenmeyer et al. 2014); this might explain these decreased Fe values during drought periods, such as for the low flow period in June–July 2018 (Fig. 3).

Even though the TOC concentration in Lake Solbergvann showed some reduction during the summer months, the TOC levels for both Lake Solbergvann and Lake Langvann were rather stable (Fig. 3). Seasonal changes in DOM properties such as molecular size, aromaticity and fluorescent characteristics were, however, significant (Figs. 4, 5). Increased intensity of photochemical and mineralization reactions during the summer season can promote the breakdown of DOM into smaller size fractions with less aromaticity. This result is supported by the increased spectral slope  $S_{275-295}$ and decreased fluorescence intensity in July (Fig. 5). The fluorescence intensity of all PARAFAC fractions decreased during the spring and summer seasons according to the fluorescence intensity. The decrease was more extensive for the fluorescence activity than for TOC for both lakes, indicating the transformation of DOM into compounds with fewer fluorophores (i.e., less aromaticity supported by increased  $S_{275-295}$ ) during the period with longer water residence time and higher temperature (March–July), a period when in-lake processes presumably are more active (Tulonen 1993).

#### Increased importance of in-lake processes

In addition to the mineralization of organically bound S, weathering of S-bearing minerals and sea salt in rainfall, previous deposition of acid rain has been a significant source of  $SO_4^{2-}$  in Østmarka. The latter source has, however, decreased severely over the past few decades (Riise et al. 2018). According to the PCA plot,  $SO_4^{2-}$  was positively related to precipitation (Fig. 6), which is in agreement with Kerr et al. (2012), who found that wetlands or saturated areas were important drivers for regional variations in  $SO_4^{2-}$ . In response to seasonal drying but opposed to Cl<sup>-</sup>,  $SO_4^{2-}$  showed a severe drop in July 2018 (Fig. 3). SO<sub>4</sub><sup>2-</sup> is to a larger extent dependent on sorption/desorption processes than Cl<sup>-</sup> (Houle and Carignan 1995), and increased adsorption of  $SO_4^{2-}$  is reported during drought periods by Singh (1984). Hence, during the drought period in the summer of 2018, there seems to be a severe retention of  $SO_4^{2-}$  in the catchments for both lakes. During rewetting periods, pools of reduced S, oxidized to  $SO_4^{2-}$  during periods with decreased water level, can be washed out (Kerr et al. 2012). For Lake Langvann and Lake Solbergvann, no extra peaks in  $SO_4^{2-}$  were noticed during rewetting. The  $SO_4^{2-}$  concentrations seemed to be reestablished in the autumn of 2018 at rather similar concentrations as previous autumn (Fig. 3). Missing peak in  $SO_4^{2-}$  may be a consequence of low sampling frequency, too high S retention in soils or the soil reservoir of available S is too small to alter the lake  $SO_4^{2-}$  concentration (as seen in Fig. 3).

Concurrently with minimum concentrations of  $SO_4^{2-}$ , there is also minimum concentrations of Fe. The minima occur somewhat earlier for Fe than for  $SO_4^{2-}$ , so there is not a synchronous relationship between these two variables. Terrestrial supply of Fe was probably greatly reduced during low flow conditions in the dry summer of 2018. This flow pattern is reasonable for a sparsely soil-covered forest catchment, such as Østmarka, which is different from peaty areas where Fe concentration may peak during low flow conditions (Heikkinen et al. 2022). In addition, lowering of the water table in Østmarka may enhance the oxic zone, promoting prevalence of ferric iron, Fe<sup>3+</sup>, with low water solubility. Much of the Fe is, therefore, thought to be retained in the



**Fig. 5** Spectral slope  $(S_{275-295}, \mu m^{-1}, \text{upper left})$ , specific UV absorption (SUVA<sub>254</sub>, L mgC<sup>-1</sup> m<sup>-1</sup>, upper right), allochthonous fluorescent DOM (Comp. 1+2, lower left) and autochthonous fluorescent DOM (Comp. 3, lower right) for Lake Langvann and Solbergvann during

reducing/oxic zone in accordance with a study by Lidman et al. (2017).

Both Fe and S are redox-sensitive elements, whose solubility is dependent on the water level. Since Fe is enriched in the lake water along with  $SO_4^{2-}$  (the oxidized form of S) during high flow conditions, there is little support for a retention of Fe sulfides, which agrees with Björnerås et al. (2022).

## **Coupling between Fe and OM**

A large part of the visible color (approximately 50%) and the UV absorption (30-40%) was related to the colloidal fraction, although significantly less than that of Fe (Table S2), where the colloidal fraction accounted for 64-84% (Fig. 4). Concerning TOC, the major part was in a L-Mw form (73-87%), a fraction that proportionally contributed less



the period from November 2017 to October 2018. The fluorescence intensities of DOM components were identified by PARAFAC modeling

to color and UV absorption but more extensively to fluorescence (L-Mw: 76–98%). These results suggest that a small fraction of OM is responsible for a large part of the color of the lakes. Except for decreasing colloidal DOM in May and July for Lake Solbergvann, relatively small seasonal variations in DOM were observed. Thus, there is no profound settling or retention of OM with season (Fig. 3). This result indicates that only a small part of DOM contributes to the colloidal Fe-DOM complex, which is most susceptible to aggregation and settling. Soil water studies from Nordic podzols also show a decoupling of Fe and DOM as a major part of Fe is enriched in deeper soil horizons than DOM (Riise et al. 2000), supporting that the flow pattern affects the transport pattern of Fe.

In-lake processes are increasing in importance when the water retention time of the lake increases because of low inflow of water. Settling of Fe, presumably as Fe hydroxides,



**Fig. 6** Principal component analysis (PCA) of key variables regulating Fe in Lake Langvann and Lake Solbergvann during the period from November 2017 to October 2018. The precipitation data used in PCA were the accumulated precipitation in the last 60 days before sampling

might therefore actively take place, supported by high pH values (Fig. 3; Neubauer et al. 2013). This is also in line with the low seasonal variability of DOM and the preferential settling of minerogenic Fe in sediments (Björnerås et al. 2021) compared to Fe-OM complexes (Herzog et al. 2020).

# Conclusion

This study shows that long-term trends and seasonal variations in Fe and DOM are different for two headwater lakes with different hydrological connectivity. Long-term increases in concentrations of Fe and decreases in concentrations of  $SO_4^{2-}$  were found for both lakes, although significant monotonic trends for Fe were found in the humic lake only. Higher concentrations of Fe and DOM were related to a lake with short water retention time in a catchment area with sparse peat cover compared to a lake with longer water retention time and thicker soil layers.

Large seasonal variations in Fe concentrations were recorded in both lakes, where minimum Fe values were found during a summer drought period in 2018. Interestingly, a concurrent decline in  $SO_4^{2-}$  was found at a time when catchment runoff was at a minimum, which suggests that the transport of both Fe and  $SO_4^{2-}$  is retained during the oxic drought episode when there is less support for formation and retention of low soluble FeS.

Compared to DOM, a large part of Fe (56-89%) was in a colloidal form (0.45 µm-10 kDa) in both lakes. Opposed to Fe, the seasonal variability in the concentration of TOC was moderate. However, using spectroscopic analyses (absorption and 3D fluorescent spectra), the properties of DOM (molecular size, aromaticity and fluorescence) showed large seasonal variations related to periods with high terrestrial DOM loading versus periods with in-lake transformation processes. A major proportion of the color contributing variables,  $a_{410}$  and Fe, was in colloidal form, suggesting that only a small fraction of DOM is responsible for a large proportion of the color in the lakes and that there is a selective retention of Fe compared to DOM fractions in lakes. Since the mobilization and retention of compounds that predominate in a colloidal fraction (e.g., Fe) are especially vulnerable to changes in flow conditions, there is a high probability of increasing Fe variations in a future climate with increased frequency of flood and drought episodes.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00027-023-00956-w.

Acknowledgements This study was supported by Taishan Scholar Foundation of Shandong Province, China (no. tsqn201909126) and Academy of Finland (grant no. 295709). It was also presented to the Nordic Centre of Excellence-Biowater (Nordforsk project no. 82263). The authors also appreciate the funding by the National Natural Science Foundation of China (no. 42103029) and the National Key Research and Development Program (no. 2021YFC3201004). The authors are grateful to Johnny Kristiansen (NMBU), Dr. Per Kristian Lunde (Oslo University Hospital, Norway) and Dr. Penghui Li (Sun Yat-Sen University) for their help with measurements and field work.

Author contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by YX and GR. The first draft of the manuscript was written by GR and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

**Funding** Open access funding provided by Norwegian University of Life Sciences.

**Data availability statement** The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

#### Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source,

provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

# References

- Björnerås C, Weyhenmeyer GA, Evans CD, Gessner MO, Grossart HP, Kangur K et al (2017) Widespread increases in iron concentration in European and North American freshwaters. Glob Biogeochem Cycles 31(10):1488–1500. https://doi.org/10.1002/ 2017GB005749
- Björnerås C, Škerlep M, Floudas D, Persson P, Kritzberg ES (2019) High sulfate concentration enhances iron mobilization from organic soil to water. Biogeochemistry 144(3):245–259. https:// doi.org/10.1007/s10533-019-00581-6
- Björnerås C, Persson P, Weyhenmeyer GA, Hammarlund D, Kritzberg ES (2021) The lake as an iron sink - new insights on the role of iron speciation. Chem Geol 584:120529. https://doi.org/10.1016/j. chemgeo.2021.120529
- Björnerås C, Weyhenmeyer GA, Hammarlund D, Persson P, Kritzberg ES (2022) Sediment records shed light on drivers of decadal iron concentration increase in a Boreal Lake. J Geophys Res Biogeosci. https://doi.org/10.1029/2021JG006670
- Feng J, Hsieh YP (1998) Sulfate reduction in freshwater wetland soils and the effects of sulfate and substrate loading. J Environ Qual 27(4):968–972. https://doi.org/10.2134/jeq1998.0047242500 2700040034x
- Heikkinen K, Saari M, Heino J, Ronkanen AK, Kortelainen P, Joensuu S et al (2022) Iron in boreal river catchments: biogeochemical, ecological and management implications. Sci Total Environ 805:150256. https://doi.org/10.1016/j.scitotenv.2021.150256
- Helms RJ, Stubbins A, Ritchie JD, Minor EC, Kieber DJ, Mopper K et al (2008) Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. Limnol Oceanogr 54(3):1023. https://doi.org/10.4319/lo.2009.54.3.1023
- Helms JR, Stubbins A, Perdue EM, Green NW, Chen H, Mopper K (2013) Photochemical bleaching of oceanic dissolved organic matter and its effect on absorption spectral slope and fluorescence. Mar Chem 155(20):81–91. https://doi.org/10.1016/j.marchem. 2013.05.015
- Helms RJ, Mao J, Stubbins A, Schmidt-Rohr K, Spencer RGM, Hernes PJ, Mopper K (2014) Loss of optical and molecular indicators of terrigenous dissolved organic matter during long-term photobleaching. Aquat Sci 76(3):353–373. https://doi.org/10.1007/ s00027-014-0340-0
- Herzog SD, Persson P, Kritzberg ES (2017) Salinity effects on iron speviation in boreal river waters. Environ Sci Technol 51:9747–9755. https://doi.org/10.1021/acs.est.7b02309
- Herzog SD, Persson P, Kvashnina K, Sofia Kritzberg E (2020) Organic iron complexes enhance iron transport capacity along estuarine salinity gradients of Baltic estuaries. Biogeosciences 17(2):331– 344. https://doi.org/10.5194/bg-17-331-2020
- Hongve D, Åkesson G (1996) Spectrophotometric determination of water colour in hazen units. Water Res 30(11):2771–2775. https:// doi.org/10.1016/S0043-1354(96)00163-7
- Hongve D, Riise G, Kristiansen JF (2004) Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water

- a result of increased precipitation? Aquat Sci 66(2):231–238. https://doi.org/10.1007/s00027-004-0708-7

- Houle D, Carignan R (1995) Role of  $SO_4$  adsorption and desorption in the long-term S budget of a coniferous catchment on the Canadian shield. Biogeochemistry 28(3):161–182
- Ingri J, Conrad S, Lidman F, Nordblad F, Engström E, Rodushkin I, Porcelli D (2018) Iron isotope pathways in the boreal landscape: role of the riparian zone. Geochimica et Cosmochimica Acta 239:49–60. https://doi.org/10.1016/j.gca.2018.07.030
- Jørgensen L, Stedmon CA, Kragh T, Markager S, Middelboe M, Søndergaardc M (2011) Global trends in the fluorescence charac- teristics and distribution of marine dissolved organic matter. Mar Chem 126(1–4):139–148. https://doi.org/10.1016/j.marchem. 2011.05.002
- Kerr JG, Eimers MC, Creed IF, Adams MB, Beall F, Burns D et al (2012) The effect of seasonal drying on sulphate dynamics in streams across southeastern Canada and the northeastern USA. Biogeochemistry 111:393–409. https://doi.org/10.1007/ s10533-011-9664-1
- Kida M, Fujitake N, Suchewaboripont V, Poungparn S, Tomotsune M, Kondo M et al (2018) Contribution of humic substances to dissolved organic matter optical properties and iron mobilization. Aquat Sci 80(3):1–11. https://doi.org/10.1007/s00027-018-0578-z
- Köhler SJ, Kothawala D, Futter MN, Liungman O, Tranvik L (2013) In-lake processes offset increased terrestrial inputs of dissolved organic carbon and color to lakes. PLoS One 8(8):1–12. https:// doi.org/10.1371/journal.pone.0070598
- Kothawala DN, Stedmon CA, Müller RA, Weyhenmeyer GA, Köhler SJ, Tranvik LJ et al (2014) Controls of dissolved organic matter quality: evidence from a large-scale boreal lake survey. Glob Change Biol 20(4):1101–1114. https://doi.org/10.1111/gcb.12488
- Kritzberg ES, Ekström SM (2012) Increasing iron concentrations in surface waters - a factor behind brownification? Biogeosciences 9(4):1465–1478. https://doi.org/10.5194/bg-9-1465-2012
- Kritzberg ES, Hasselquist EM, Škerlep M, Löfgren S, Olsson O, Stadmark J et al (2020) Browning of freshwaters: consequences to ecosystem services, underlying drivers, and potential mitigation measures. Ambio 49(2):375–390. https://doi.org/10.1007/ s13280-019-01227-5
- Li P, Hur J, Hur L, Hur J (2017) Utilization of UV-Vis spectroscopy and related data analyses for dissolved organic matter (DOM) studies: a review. Crit Rev Environ Sci Technol 47(3):131–154. https://doi. org/10.1080/10643389.2017.1309186
- Lidman F, Boily Å, Laudon H, Köhler SJ (2017) From soil water to surface water-how the riparian zone controls element transport from a boreal forest to a stream. Biogeosciences 14(12):3001–3014. https://doi.org/10.5194/bg-14-3001-2017
- Laudon H, Berggren M, Ågren A, Buffam I, Bishop K, Grabs T, Jansson M, Köhler S (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
- Mattsson T, Kortelainen P, Räike A (2005) Export of DOM from boreal catchments: impacts of land use cover and climate. Biogeochemistry 76(2):373–394. https://doi.org/10.1007/s10533-005-6897-x
- Murphy KR, Stedmon CA, Graeber D, Bro R (2013) Fluorescence spectroscopy and multi-way techniques. PARAFAC. Anal Methods 5(23):6557. https://doi.org/10.1039/c3ay41160e
- Neubauer E, Köhler SJ, von der Kammer F, Laudon H, Hofmann T, Neubauer E et al (2013) Effect of pH and stream order on iron and arsenic speciation in boreal catchments. Environ Sci Technol 47(13):7120–7128. https://doi.org/10.1021/es401193j
- Norwegian Standard Association (2002) NS 4787 water quality. Determination of colour. Method by spectrophotometric determination of absorbance at 410 nm, 2nd edn. Norwegian Standards, Oslo

- Raiswell R, Canfield DE (2012) The iron biogeochemical cycle past and present. Geochem Perspect 1(1):1–232. https://doi.org/10. 7185/geochempersp.1.1
- Read JS, Rose KC (2013) Physical responses of small temperate lakes to variation in dissolved organic carbon concentrations. Limnol Oceanogr 58(3):921–931. https://doi.org/10.4319/lo.2013.58.3. 0921
- Riise G, Salbu B, Vogt RD, RanneklevMykkelbost SBTC (1994) Mobility of humic substances, major and minor elements in lake Skjervatjern and its catchment area. Environ Int 20(3):287–298. https://doi.org/10.1016/0160-4120(94)90112-0
- Riise G, Van Hees P, Lundström U, Tau Strand L (2000) Mobility of different size fractions of organic carbon, Al, Fe. Mn and Si in Podzols Geoderma 94(2–4):237–247. https://doi.org/10.1016/ S0016-7061(99)00044-0
- Riise G, Müller RA, Haaland S, Weyhenmeyer GA (2018) Acid rain strong external driver that has suppressed water colour variability between lakes. Boreal Environ Res 23:69–81
- Ruttner F (1953) Fundamentals of limnology, 3rd edn. University of Toronto Press
- Salmi T, Määttä A, Anttila A, Ruojo-Airola T, Amnell T (2002) Detecting trends of annual values of atmospheric pollutants by the Mann–Kendall test and Sen's slope estimates–the Excel template application MAKESENS. Finnish Meteorological Institute
- Singh BR (1984) Sulfate sorption by acid forest soils: 2. Sulfate adsorption-isotherms with and without organic-matter and oxides of aluminum and iron. Soil Sci 138(4):194–297
- Stedmon CA, Bro R (2008) Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. Limnol Oceanogr Methods 6(11):572–579. https://doi.org/10.4319/lom. 2008.6.572

- Stedmon CA, Markager S (2005) Resolving the variability of dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis. Limnol Oceanogr. https://doi.org/ 10.4319/lo.2005.50.2.0686
- Temnerud J, Düker A, Karlsson S, Allard B, Bishop K, Fölster J, Köhler S (2013) Spatial patterns of some trace elements in four Swedish stream networks. Biogeosciences 10(3):1407–1423. https://doi.org/10.5194/bg-10-1407-2013
- Tulonen T (1993) Bacterial production in a mesohumic lake estimated from [14C]leucine incorporation rate. Microb Ecol 26(3):201– 217. https://doi.org/10.1007/BF00176953
- Vuori KM (1995) Direct and indirect effects of iron on river ecosystems. Ann Zool Fenn 32(3):317–329
- Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37(20):4702–4708. https:// doi.org/10.1021/es030360x
- Weyhenmeyer GA, Prairie YT, Tranvik LJ (2014) Browning of boreal freshwaters coupled to carbon-iron interactions along the aquatic continuum. PLoS One. https://doi.org/10.1371/journal.pone. 0088104
- Xiao Y, Riise G (2021) Coupling between increased lake color and iron in boreal lakes. Sci Total Environ 767:145104. https://doi.org/10. 1016/j.scitotenv.2021.145104

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.