



High sulfate concentration enhances iron mobilization from organic soil to water

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Abstract Widespread increases in iron (Fe) concentrations are contributing to ongoing browning of northern freshwaters, but the driver/s behind the trends are not known. Fe mobilization in soils is known to be controlled by redox conditions, pH, and DOC availability for complexation. Moreover, high sulfate concentrations have been suggested to constrain Fe in transition from soil to water, and declining sulfate deposition to have the opposite effect. We studied the effect of these Fe mobilization barriers in a microcosm experiment, applying high (peak S deposition) and low (present day) sulfate treatments and oxic versus anoxic conditions to boreal (O horizon) soil slurries. We hypothesized that anoxic conditions would favor Fe

release. On the contrary we expected high sulfate concentrations to suppress Fe mobility, through FeS formation or by lowering pH and thereby DOC concentrations. Anoxia had positive effects on both Fe and DOC concentrations in solution. Contrasting with our hypothesis, Fe concentrations were enhanced at high sulfate concentrations, i.e. increasing acidity in high sulfate treatments appeared to promote Fe mobilization. Establishment of the basidiomycete fungus *Jaapia ochroleuca* in the oxic treatments 44 days into the experiment had a major impact on Fe mobilization by increasing total Fe concentrations in solution. Thus, anoxia and acidity, along with fungi mediated mobilization, were important in controlling Fe release from soil to the aqueous phase. While Fe is often assumed to precipitate as Fe(oxy)hydroxides in the transition from anoxic to oxic water in the riparian zone, Fe from anoxic treatments remained in solution after introduction of oxygen. Our results do not support reduced atmospheric S deposition as a driver behind increasing Fe concentrations in boreal freshwaters, but confirm the importance of reducing conditions—which may be enhanced by higher soil temperature and moisture—for mobilization of Fe across the terrestrial-aquatic interphase.

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Introduction

Iron (Fe) concentrations in boreal freshwaters in Northern Europe are on the rise, and the increase is happening at a high rate. Björnerås et al. (2017) reported significantly positive trends for Fe in 39% out of 213 North European waterbodies analyzed, and that the median increase was 61% during the period 1990–2013. These striking trends in Fe concentrations are contributing to the ongoing browning of freshwaters (Kritzberg and Ekstrom 2012; Weyhenmeyer et al. 2014). Fe is also known to influence the mobilization and bioavailability of phosphorus (Bakker et al. 2016), and has been suggested to exert a major control on carbon (C) sequestration by affecting flocculation, sedimentation, and preservation of organic C in sediments (von Wachenfeldt et al. 2008; Lalonde et al. 2012). Thus, given the important role of Fe in freshwater systems, it is imperative to understand the underlying driver/s of the rising Fe concentrations.

The main sources of Fe to aquatic systems are the surrounding catchment soils (Nurnberg and Dillon 1993). Although Fe is prevalent in the earth crust, the low solubility of Fe(III), which prevails under oxic conditions and neutral pH, restricts mobility (Stumm and Morgan 1996). Weathering of mineral components of the soil is the first step of Fe mobilization (Giesler et al. 2000). The chemical weathering is enhanced by acidifying compounds of various origins, including organic acids from vegetation and microbes (Drever 1994; Chen et al. 2000; Landeweert et al. 2001). Since positive trends in Fe concentrations were more frequently found in catchments with coniferous forest, land-use changes and expanding forestry may contribute to enhanced Fe export to freshwaters (Björnerås et al. 2017). Coniferous forests have been shown to enhance weathering rates and mineral fluxes to boreal rivers (Humborg et al. 2004). In podzols, which are the typical soils of coniferous boreal forests, Fe and organic acids are enriched in the surface (O/A) horizons (Giesler et al. 2000). Metal–organic acid complexes are eluviated from the acidic surface horizons and precipitated in response to the higher pH and decreased solubility in the subsoil (B horizon) (Bergkvist 1987; Lundstrom et al. 2000). From such soil horizons, Fe can be transported with discharging groundwater entering boreal headwaters (Ledesma et al. 2013; Lidman et al. 2017). The mobilization of Fe from soils largely requires either association to

organic matter (OM) (Jansen et al. 2004), reducing conditions induced by oxygen deficiency (Grybos et al. 2009), or low pH (Kuesel et al. 2001). Reducing conditions promoting microbial Fe(III) reduction (Lovley 1991), and hence the release of the more mobile Fe(II) from hydrologically connected soils, has been suggested to exert a major control on Fe concentrations in boreal freshwaters (Sarkkola et al. 2013; Ekstrom et al. 2016; Björnerås et al. 2017). Also, reducing conditions induced by high temperatures and soil moisture stimulate the formation of organic acids that co-transport Fe from soils to adjacent streams (Bergkvist 1987). Hence, pH and redox conditions, as well as concentration and properties of OM control Fe mobilization in soils. Studies of Fe mobilization from soils to water have traditionally focused on bacterial or abiotic processes, but more recent studies point also to the potential importance of fungi (Clarholm and Skjellberg 2013). The transition from soil to stream, which often includes sharp gradients in these particular factors (Lidman et al. 2017), may represent a second “mobilization barrier” of Fe.

Redox mobilization of Fe may be modulated by the presence of other electron acceptors. For instance, the availability of nitrate (NO_3^-) as a competing electron acceptor in soils has been suggested to affect Fe mobilization. Musolff et al. (2017) linked increasing Fe concentrations in mountain streams in Germany to declining atmospheric nitrogen deposition, arguing that the diminishing importance of NO_3^- as a competing electron acceptor has enhanced Fe reduction and mobilization.

Another potentially competing electron acceptor in soils is sulfate (SO_4^{2-}), and the sharp reduction in atmospheric sulfur (S) deposition since the mid 1980s has been suggested to potentially shift anaerobic respiration from SO_4^{2-} to Fe reduction (Knorr 2013), and thereby to enhance Fe mobilization. The high availability of S during phases of high S deposition may potentially also have suppressed Fe mobility in soils by formation and precipitation of stable Fe sulfides (FeS) (Bottrell et al. 2007; Knorr et al. 2009; Knorr 2013). Moreover, the low pH associated with high S deposition potentially increased the solubility of Fe minerals, yet suppressed the solubility of high molecular weight DOC (Ekstrom et al. 2011) and thus the solubility of Fe–DOC associations. Hence, assessing the effect of changing S deposition on Fe mobility

in soils is not trivial given the potential influence of mobilization mechanisms acting in opposite directions. For instance, the indirect effect of pH via DOC may be more important for Fe solubility than the direct effect of pH. Along with a reduction in S deposition a recovery from acidification has followed in many catchments and SO_4^{2-} concentrations in surface waters have generally declined (Schopp et al. 2003; Garmo et al. 2014). A correlation between falling SO_4^{2-} concentrations and rising DOC concentrations across lakes in Northern Europe and North America, suggests that a recovery from acidification may be one underlying driver of frequent trends of increasing DOC (Monteith et al. 2007). A similar relationship was found for increasing Fe concentrations and declining SO_4^{2-} concentrations in freshwaters (Björnerås et al. 2017), but the underlying mechanism behind such a relationship is poorly understood.

The aim of this study was to experimentally examine the effect of SO_4^{2-} and oxygen on mobilization of Fe from an organic soil. We hypothesized that anoxic conditions would favor the release of Fe by reductive dissolution, but that high availability of SO_4^{2-} would hamper the release of Fe, by formation of FeS, competition by SO_4^{2-} as an electron acceptor, or by high acidity reducing the DOC available for Fe complexation. These hypotheses were tested in a microcosm experiment with crossed treatments of high (peak S deposition) and low (present day) SO_4^{2-} treatments and oxic versus anoxic conditions. Additionally, we tested if Fe mobilized under reducing conditions would be stable against precipitation under oxygenated conditions, relating to the transition zone between hydrologically connected soils and surface waters.

In this study, unexpectedly, growth of the wood decaying fungus *Jaapia ochroleuca* was found in the oxic treatments 7 weeks into the experiment. The establishment of this fungus was paralleled by a marked change in soil water chemistry. We exploited this unintended event as it likely lowered oxygen concentrations and introduced organic and carbonic acids. By comparing the chemistry before and after the fungus was established we could assess the effect on Fe mobilization.

Methods

Soil sampling

Soil was sampled at the Asa Experimental Forest and Research Station in southern Sweden (57°08'N, 14°45'E, alt. 190–200 m.a.s.l.). The site is dominated by Norway spruce (*Picea abies*) with the present stand planted in 1967. Annual mean precipitation in the area is 688 mm, yearly mean temperature is 5.5 °C, and the average length of the growing season is 190 days (Kleja et al. 2008). The bedrock consists of granites and porphyries covered with sandy till (sand 55%, silt 42% and clay 3%) (Berggren et al. 2004). Soil at the sampling site is a podzol with an O-horizon of 3–10 cm depth with a total carbon pool of 4.3 kg m⁻² (Froberg et al. 2005).

Soil was sampled from a location where plots were subjected to an irrigation experiment to study the effect of acid deposition on DOC concentration and chemical character using the same SO_4^{2-} regimes as in the present work (Ekstrom et al. 2011). Soil from the O horizon was collected, excluding surface litter, and directly sieved through a coarse sieve. The soil was left to air-dry for 3 days before it was sieved through a 2-mm sieve and left to dry for another 2 days. Before dividing the soil between microcosms it was homogenized. The soil had a $\text{pH}_{\text{H}_2\text{O}}$ of 3.45 (soil to water ratio 1:4 wt:wt), consisted mainly of OM (78%), and contained 41.4, 106, 0.85, and 31.3 $\mu\text{mol g}^{-1}$ of Fe, Al, Mn, and S respectively.

Microcosm experiment

Pyrex bottles (1.2 L) were used for the microcosms, to which 110 g dry soil and 1.1 L of artificial rainwater were added. Soil slurries were exposed to two levels of SO_4^{2-} concentration and oxic versus anoxic conditions in a 2 by 2 design to test the effect on Fe mobilization. Each treatment was run in four replicates, resulting in 16 microcosms in total. The two SO_4^{2-} treatments were chosen to represent precipitation with current levels of SO_4^{2-} (LS) and levels representative for peak S deposition in the 1980s (HS). The artificial rainwater was prepared according to Ekstrom et al. (2011). The two different SO_4^{2-} treatments contained 0.012 and 0.36 mM H_2SO_4 , respectively. pH was 6.74 in the LS and 3.35 in the HS

treatment water, which is within the range of pH measured in throughfall in southern Sweden spruce forest during peak acidification (Bergkvist 1986; Sanden et al. 1987; Pålsson and Bergkvist 1995). Each SO_4^{2-} treatment was run under oxic (O) and anoxic (A) conditions.

Anoxic replicates were sealed with rubber lids, which had 6-mm tubes sealed with valves inserted through them, so that sampling was possible without introduction of oxygen. One of the tubes reached halfway into the soil solution to enable sampling while the other end of the tube had its opening in the air pocket at the top of the bottle. Oxic replicates were left open, to enable steady-state oxygen conditions in the soil solutions. All the material and sampling equipment were acid washed before the start of the experiment, with reusable equipment also being acid washed before every sampling. The microcosms were mixed and placed on a rotation table (45 rpm), where they were incubated in darkness in a temperature-controlled room (20 °C).

The experiment ran for 134 days, during which time sampling was conducted on 15 occasions. A 20-mL syringe was used for sampling. When sampling anoxic samples the syringe was attached to the valves, while a tube was attached to the syringe for the oxic samples. From the anoxic treatments, a small volume was discarded at each sampling to get rid of the water in the sampling tube. Two 20-mL samples were taken from each replicate; the first was immediately used for measuring oxygen (O_2), redox potential (Eh) and pH. The second sample was filtered (GF/F, Whatman, pore size: 0.7 μm), split into two 20-mL plastic vials and stored frozen for later analyses of total Fe, Fe(II), Mn, Al, SO_4^{2-} , NO_3^- , PO_4^{3-} and DOC concentrations. Thus, the phase that was analyzed to assess mobilization from soil may also have contained suspended particles < 0.7 μm . After sampling the volume was replaced by adding the rainwater according to the assigned treatment. Losses by evaporation were replaced so that the volume was kept constant throughout the experiment. For anoxic samples artificial rainwater was nitrogen bubbled for 15 min before addition.

Fungal identification

Part of the fruitbody of the fungal species that grew on the surface of the submerged soil was collected and

air-dried for a week. A small section of the dried sample was placed on a glass slide, and the tissue was stained with a 1.5% Phloxine B solution, followed by addition of a small amount of 2% KOH solution. A second section was stained using a small amount of Melzer solution. The sections were examined using an inverted microscope (Nikon DIAPHOT 300), for the presence of basidia, clamp connections, spores, and cystidial elements. About thirty basidiospores were measured. Photographs of the microscopic characteristic of the fungus were acquired using a DMK 33UX174 digital camera.

Re-oxidation experiment

To test to what extent filterable Fe from anoxic treatments would remain in solution after oxygenation a re-oxidation experiment was performed. On day 83, 40 ml of soil solution was removed from the anoxic microcosms and filtered through GF/F filter. A subsample of 10 mL was immediately fixed for Fe analysis and the remaining sample was transferred into 50-mL Falcon tubes. These were then left open on a rotation table (45 rpm) for 48 h to allow oxygenation. After this, samples were centrifuged (3000 rcf) for 8 h at 4 °C to separate particles from the suspension. The supernatant of each sample was analyzed for Fe and compared to concentrations before oxidation.

Analytical methods

Total Fe, Mn, and Al concentrations were analyzed with ICP-OES (Perkin Elmer Optima 8300). For metal analyses, soil solution samples were acidified (1% HNO_3) 24 h before analysis, while a soil sample was extracted in 7 M HNO_3 and measured according to SS 28311 (2017). A subset of samples representing the beginning of the experiment (day 3), before the fungus was detected (day 16), and after the fungus had established in the oxic microcosms (day 73) were analyzed by the Ferrozine method for Fe(II) (Viollier et al. 2000). Absorbance of the Ferrozine solutions were recorded at 562 nm on a Beckman DU 800 Coulter spectrophotometer. SO_4^{2-} , NO_3^- , and PO_4^{3-} concentrations were analyzed with Ion chromatography (816 Advanced Compact IC, Metrohm).

A Unisense Microsensor Multimeter (Version 2.01) attached with several electrodes was used for measurements of O_2 (OX-100; Unisense), H_2S (H₂S-100;

Unisense) and redox potential (RD-100; Unisense). Since the H₂S electrode did not produce a stable and reliable signal, results for this electrode are not presented. For pH measurements a 913 pH Meter (Metrohm) was used.

DOC concentrations were analyzed on a Shimadzu TOC V-CPN analyzer, using the non-purgeable organic matter method (NPOC). Soil OM content was determined by loss of ignition (LOI) at 400 °C during 8 h.

Statistics

The treatment effects on all continuously measured variables (O₂, pH, redox, total Fe, Al, Mn, SO₄²⁻, DOC, NO₃⁻ and PO₄³⁻) were investigated using two-way repeated measures ANOVAs. To correct for violations of sphericity, Greenhouse–Geisser corrections were applied. The data from the period when no fungi were detected (NF, day 1–44) and the period with fungi established in the oxic treatments (WF, day 44–134) were analyzed separately. During NF, the influence of SO₄²⁻ concentration and oxic versus anoxic conditions on the response variables could be assessed. By comparing the influence on the response variables between NF and WF the effect of the fungus could be evaluated. Differences in Fe concentration between the O and A treatments at the end of the experiment (day 134), as well as differences in Fe(II) concentrations between treatments for day 3, 16, and 73, were analyzed using a Two-Way ANOVA. Differences in Fe concentration between anoxic and re-oxidized samples were tested by paired samples *t* test. All statistical analyses were performed with IBM SPSS Statistics v.25 and plots were created with GraphPad Prism v.7.

Results

Experimental conditions

The targeted experimental conditions were achieved regarding O₂ and SO₄²⁻ concentrations (Fig. 1). A sharp decline in dissolved O₂ was observed in all treatments during the first days of the experiment, probably as a result of strongly enhanced microbial activity (Fig. 1a). Well-oxygenated conditions were established after 3 days in the assigned oxic treatments, while low and stable O₂ conditions prevailed in

the anoxic treatments throughout the experiment (Fig. 1a). Accordingly, O₂ concentrations were significantly higher in the oxic than in the anoxic treatments ($F = 1.50 \times 10^3$, $p < 0.001$), and did not differ between S treatments ($F = 0.78$, $p = 0.39$). The oxic treatments were not saturated with oxygen, but dissolved oxygen was on average 73% compared to 4% in the anoxic treatments. Redox potential measurements reflected differences in O₂ concentration with lower redox potential in the sealed (357 ± 85.1 mV) than in the open microcosms (481 ± 64.1 mV) ($F = 400$, $p < 0.001$).

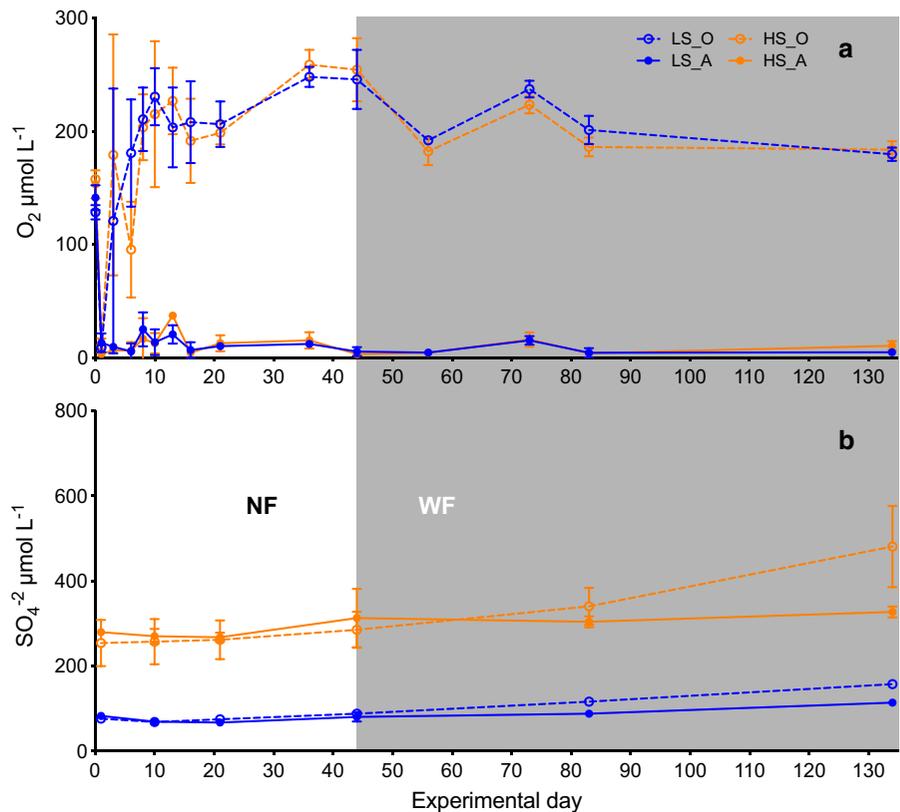
The HS treatments had significantly higher SO₄²⁻ concentration than the LS treatments throughout the experiment ($F = 365$, $p < 0.001$), while there was no difference in SO₄²⁻ between oxic and anoxic treatments ($F = 0.08$, $p = 0.78$).

On day 44, growth of fungal mycelium on the submerged litter was detected in the oxic treatments. The growth continued until the mycelium formed a thick cover on the litter material. Examination of this tissue under the microscope revealed that the hyphae had clamp connections and therefore, belonged to a basidiomycete fungus (Fig. S1). Further examination of the tissue revealed that it represented a fruitbody of *Jaapia ochroleuca* (Bres.) Nannf. & J. Erikss. based on the characteristics of the basidiospores (fusiform to narrowly ellipsoid, slightly thick-walled, $11.2 - 15.4 \times 4.1 - 5.7$ μm, however, not obviously dextrinoid) and the cystidia (tubular, at least 100 μm long, with thickening cell wall towards the base). The experimental period before and after day 44, when the fungus was noticed are termed NF and WF (no fungus and with fungus), respectively.

Effect of presence/absence of oxygen and S availability on Fe mobilization (NF)

The pH at the start of the experiment was on average $3.45 (\pm 0.04)$ and $3.61 (\pm 0.01)$, in the HS and LS treatments respectively, and $3.64 (\pm 0.09)$ and $3.81 (\pm 0.09)$ at day 44, (Fig. 2a). Thus pH was significantly lower in HS than LS ($F = 205$, $p < 0.001$). Moreover, pH was somewhat lower in the anoxic than the oxic treatments ($F = 7.21$, $p < 0.05$). During this part of the experiment pH increased in all treatments ($F = 33.2$, $p < 0.001$). The lack of interaction between time and the treatment factors indicate that the increase in pH did not differ across treatments

Fig. 1 Mean dissolved oxygen [O_2] (a) and sulfate [SO_4^{2-}] (b) concentration in the four treatments over time. *HS* high sulfuric acid treatments, *LS* low sulfuric acid treatments, *O* oxic treatments, and *A* anoxic treatments. Error bars ± 1 SD. *NF* (white background) and *WF* (grey background) highlight the period before and after the influence of fungal growth in the *O* treatments



($F_{\text{time} \times O_2} = 2.13$, $p_{\text{time} \times O_2} = 0.09$, and $F_{\text{time} \times SO_4} = 2.64$, $p_{\text{time} \times SO_4} = 0.05$).

Both total Fe and DOC concentrations increased in all treatments over time (Fig. 2b, c; $F_{\text{Fe}} = 184$, $p_{\text{Fe}} < 0.001$, and $F_{\text{DOC}} = 181$, $p_{\text{DOC}} < 0.001$ respectively). Initial total Fe concentration was on average $3.8 (\pm 0.5) \mu\text{mol L}^{-1}$ and on day 44 it was $8.3 (\pm 3.2)$ and $15.7 (\pm 4.0) \mu\text{mol L}^{-1}$ in the oxic and anoxic treatments, respectively. Thus, as hypothesized, lack of oxygen had a significantly positive effect on Fe ($F = 70.4$, $p < 0.001$), although the increase in total Fe concentration was small. However, total Fe concentrations in solution were not lower in HS than in LS as hypothesized, but instead higher ($F = 14.5$, $p < 0.01$). The rate of increase in total Fe was significantly different between both O_2 and SO_4 treatments ($F_{\text{time} \times O_2} = 29.9$, $p_{\text{time} \times O_2} < 0.001$, and $F_{\text{time} \times SO_4} = 19.4$, $p_{\text{time} \times SO_4} < 0.001$). At day 3 Fe(II) concentrations were independent of both O_2 and SO_4 treatments (Fig. 3) ($F_{O_2} = 0.95$, $p_{O_2} = 0.36$, and $F_{SO_4} = 1.26$, $p_{SO_4} = 0.30$). On day 16 however, Fe(II) concentrations were positively affected by A and HS

conditions ($F_{O_2} = 181$, $p_{O_2} < 0.001$, and $F_{SO_4} = 13.0$, $p_{SO_4} < 0.01$). The mean dissolved Fe to S molar ratio was 7.11×10^{-2} for the LS treatments and 2.48×10^{-2} for the HS treatments.

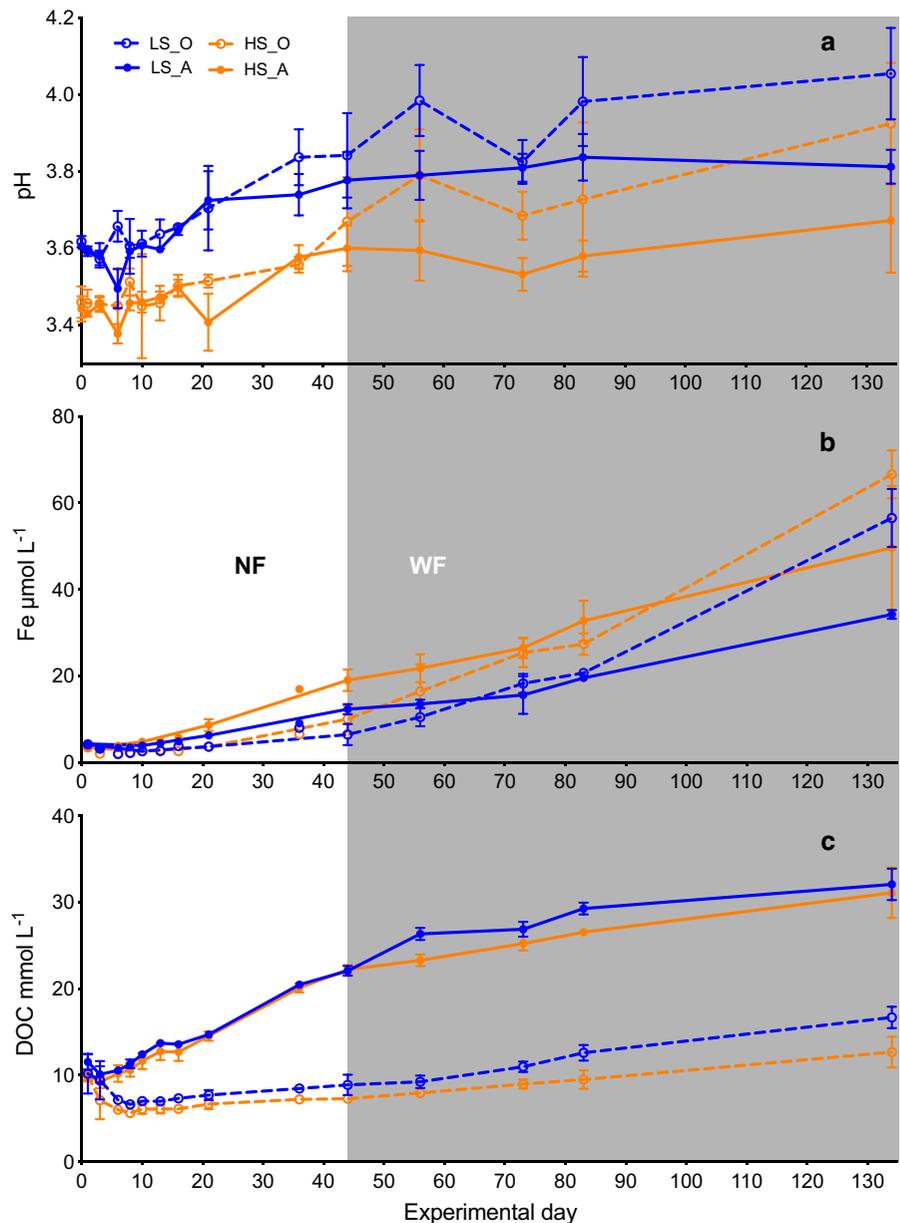
The DOC concentration started at $10.4 (\pm 1.4) \text{mmol L}^{-1}$ and increased to higher levels in the anoxic treatments ($22.2 \pm 0.5 \text{mmol L}^{-1}$) than in the oxic treatments ($8.1 \pm 1.2 \text{mmol L}^{-1}$; $F = 520$, $p < 0.001$). Moreover, mean DOC concentrations were significantly higher in LS than HS ($F = 10.7$, $p < 0.01$). The lack of interaction between time and S ($F_{\text{time} \times SO_4} = 0.65$, $p_{\text{time} \times SO_4} = 0.58$) and significant time $\times O_2$, ($F_{\text{time} \times O_2} = 160$, $p_{\text{time} \times O_2} < 0.001$) indicate that the response in DOC to the O/A treatment was independent of SO_4^{2-} concentration (Fig. 2c).

The Fe:DOC ratio was low in all treatments, although slightly higher in the oxic than in the anoxic treatments (5.5×10^{-4} and 4.6×10^{-4} respectively).

Mobilization of Fe in presence of fungi (WF)

During this period (day 44–134), hyphae covered the soil of the microcosms of the *O* treatments, and formed

Fig. 2 Mean pH (a), Fe concentration (b), and DOC concentration (c) in the four treatments over time. *HS* high sulfuric acid treatments, *LS* low sulfuric acid treatments, *O* oxic treatments, and *A* anoxic treatments. Error bars ± 1 SD. NF (white background) and WF (grey background) highlight the period before and after the influence of fungal growth in the O treatments



a layer that was approximately 0.5 cm thick at the end of the experiment. When the experiment was terminated, oxygen concentrations were measured in the fungal layer and in the soil below, revealing low concentrations in the fungal cover, and anoxic conditions in the soil (results not shown). Thus, the high O_2 concentrations of the O treatments measured also after day 44, represent only the volume above the fungal layer.

During WF, pH continued to increase in all treatments ($F = 6.33$, $p < 0.01$), and was highest in LS_O throughout the experiment (Fig. 2a). Total Fe and DOC concentrations continued to rise too in all treatments ($F_{\text{Fe}} = 252$, $p_{\text{Fe}} < 0.001$, $F_{\text{DOC}} = 164$, $p_{\text{DOC}} < 0.001$) with total Fe concentrations being significantly higher in HS than in LS while the pattern remained the opposite for DOC during WF ($F_{\text{Fe}} = 34.7$, $p_{\text{Fe}} < 0.001$, $F_{\text{DOC}} = 31.8$, $p_{\text{DOC}} < 0.001$). However, while DOC concentrations were higher in

the A treatments throughout the experiment there was no longer a significant difference in total Fe between the O and A treatments ($F_{\text{DOC}} = 1992$, $p_{\text{DOC}} < 0.001$, $F_{\text{Fe}} = 0.81$, $p_{\text{Fe}} = 0.39$). Instead, Fe release from the O treatments with fungi exceeded those in the anoxic microcosms at the end of the experiment ($F = 22.0$, $p < 0.01$). On day 73 there was an interaction between O_2 and SO_4 treatments on Fe(II) (Fig. 3) ($F_{\text{O}_2 \times \text{SO}_4} = 14.3$, $p_{\text{O}_2 \times \text{SO}_4} < 0.01$). Testing the effect of O_2 treatments as a single factor, Fe(II) concentrations were significantly higher in A compared to O treatments ($F_{\text{O}_2} = 12.4$, $p_{\text{O}_2} < 0.01$).

Overall, only a small fraction of the Fe pool was mobilized in the soil during the experiment. From the 4.6 mmol Fe that was available in each microcosm initially, between 0.9 (LS_A) and 1.7% (HS_O) was detected in solution on day 134.

Other element fluxes

Both Al and Mn concentrations were highest in HS_A throughout the experiment and appeared unaffected by the growth of fungi in the O treatments (Fig. 4). Mn mobilization was enhanced in the A and HS treatments during NF ($F_{\text{O}_2} = 9.67$, $p_{\text{O}_2} < 0.01$, and $F_{\text{SO}_4} = 156$, $p_{\text{SO}_4} < 0.001$), as well as during WF ($F_{\text{O}_2} = 9.69$, $p_{\text{O}_2} < 0.05$, and $F_{\text{SO}_4} = 145$, $p_{\text{SO}_4} < 0.001$), although Mn concentrations in O exceeded those in A towards the end of the experiment, as indicated by the significant interaction between treatment factors during WF ($F_{\text{O}_2 \times \text{SO}_4} = 7.02$, $p_{\text{O}_2 \times \text{SO}_4} < 0.05$). For Al, significant interactions between treatment factors during both NF and WF show that treatment effects were not consistent throughout the experiment (NF:

$F_{\text{O}_2 \times \text{SO}_4} = 57.0$, $p_{\text{O}_2 \times \text{SO}_4} < 0.001$, WF: $F_{\text{O}_2 \times \text{SO}_4} = 96.1$, $p_{\text{O}_2 \times \text{SO}_4} < 0.001$).

NO_3^- concentrations dropped in the four treatments until day 10 and stayed low during NF (Fig. 5a). Accordingly, there was no significant difference in NO_3^- between the O and S treatments ($p_{\text{O}_2} > 0.05$). The presence of fungi may have had a negative effect on NO_3^- concentration, since concentrations were significantly higher in A compared to O, while there was no significant difference between LS and HS ($F_{\text{O}_2} = 7.74$, $p_{\text{O}_2} < 0.05$, $F_{\text{SO}_4} = 1.75$, $p_{\text{SO}_4} = 0.21$). In contrast, PO_4^{3-} concentrations increased during WF and there was no significant difference between treatments ($p > 0.05$) (Fig. 5b). During NF, higher PO_4^{3-} was detected in LS compared to HS and in A compared to O ($F_{\text{O}_2} = 9.45$, $p_{\text{O}_2} < 0.05$, and $F_{\text{SO}_4} = 15.0$, $p_{\text{SO}_4} < 0.01$).

Re-oxidation experiment

When water samples from the anoxic treatments at day 83 were allowed to oxidize, no loss of Fe from solution was observed, i.e. total Fe concentrations in the re-oxidized samples were not lower than the anoxic samples ($t = 2.30 \times 10^{-2}$, $p = 0.98$).

Discussion

Redox-driven Fe mobilization from soil to water—the role of O_2

The desired experimental conditions were achieved early on with SO_4^{2-} and pH levels corresponding to

Fig. 3 Mean Fe(II) concentration in the four treatments over time. HS high sulfuric acid treatments, LS low sulfuric acid treatments, O oxie treatments, and A anoxic treatments. Error bars ± 1 SD. NF (white background) and WF (grey background) highlight the period before and after the influence of fungal growth in the O treatments

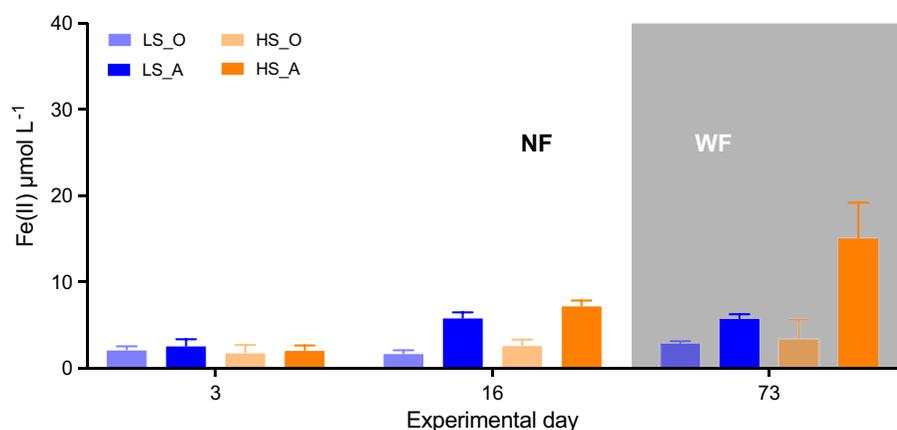
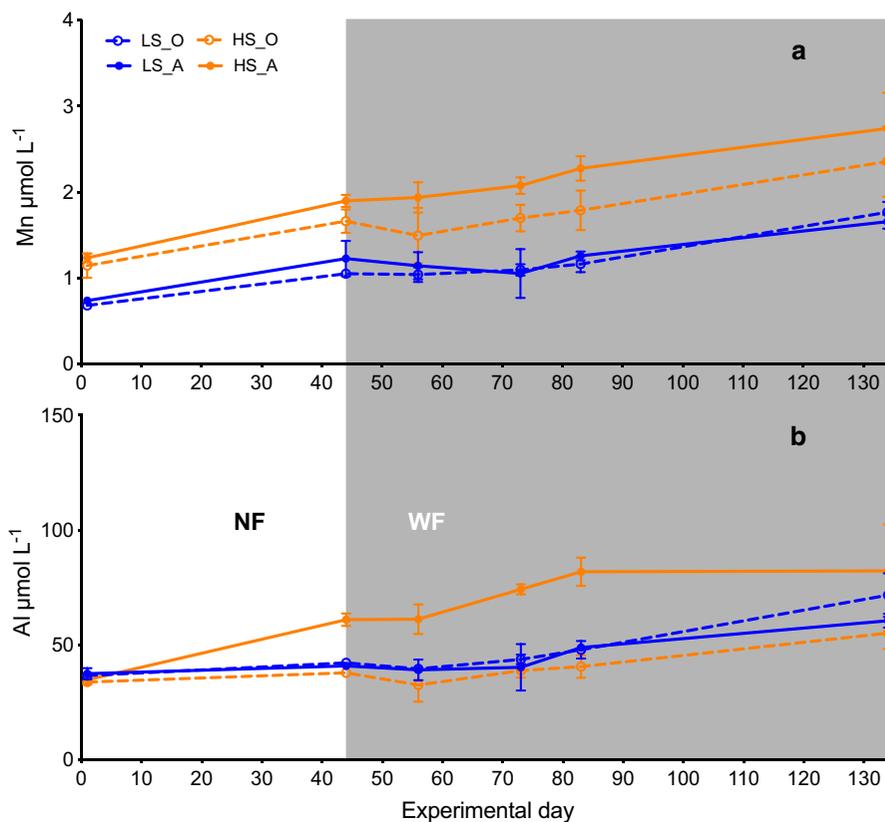


Fig. 4 Mean Mn (a), and Al concentration (b) in the four treatments over time. *HS* high sulfuric acid treatments, *LS* low sulfuric acid treatments, *O* oxic treatments, and *A* anoxic treatments. Error bars ± 1 SD. NF (white background) and WF (grey background) highlight the period before and after the influence of fungal growth in the *O* treatments

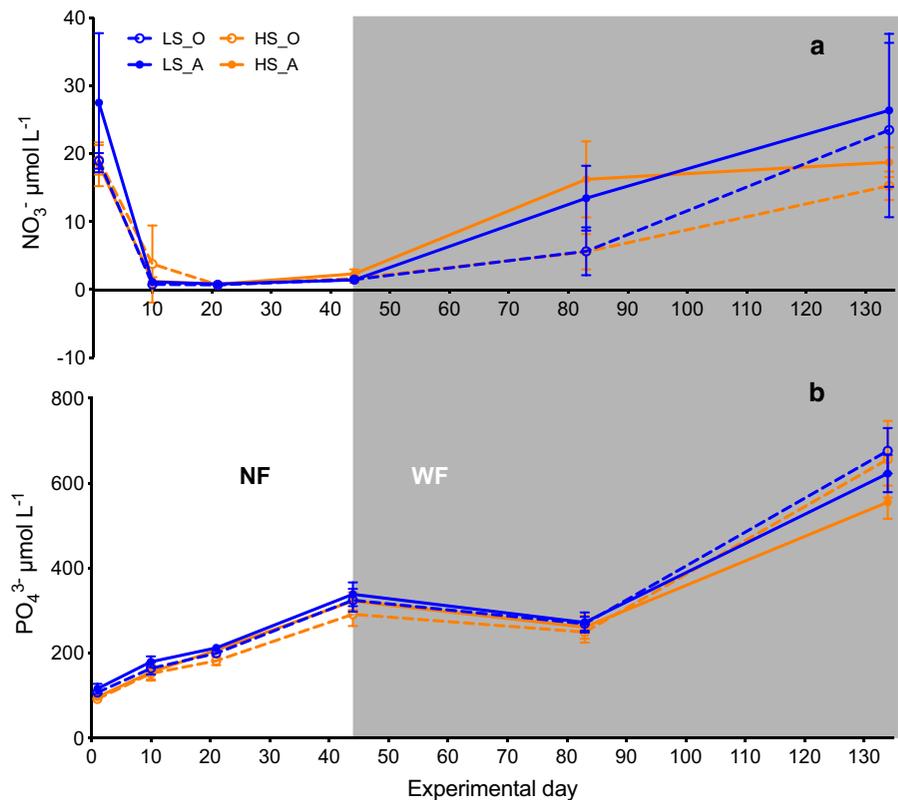


those found in throughfall in the 1980s (HS) and at the present (LS) (Ekstrom et al. 2011). The water in the open microcosms was high in dissolved oxygen, while in the sealed microcosms oxygen was rapidly consumed. As expected, Fe mobilization was favored by anoxic conditions and total Fe concentrations in solution were roughly twofold higher in anoxic compared to oxic treatments at day 44. Reductive dissolution of Fe(III) to Fe(II) was likely contributing to the higher total Fe concentrations in the anoxic treatments, considering that reducing conditions—i.e. $E_h < 500$ mV at pH 4 (Takeno 2005)—prevailed in the anoxic treatments. This is supported by the higher Fe(II) concentrations in the anoxic treatments. Furthermore, reductive dissolution may have contributed to the more moderate rise in Fe over time in the oxygenated microcosms as well, given that there may be heterogeneity with suboxic microenvironments and that the average redox potential was fairly low (mean $E_h = 481$ mV). However, increases in total Fe concentrations over time does not necessarily derive solely from Fe(III) reduction but could also be due to

non-reductive extraction of Fe complexed by organic matter. Interestingly, only a minor fraction of the total Fe pool was mobilized ($< 2\%$), demonstrating that most Fe was in a form not readily available for dissolution, potentially in mineral grains mixed into the organic layer (Giesler et al. 2000).

DOC concentrations were also significantly higher in the anoxic treatments, potentially due to higher mineralization rates in the oxic treatments, as well as due to OM solubilization under reducing conditions (Grybos et al. 2009). Sorption of DOC to metal oxides (including (oxy)hydroxides) in soils have been suggested to be an important mechanism contributing to the preservation of soil OC (Kaiser and Guggenberger 2000), as well as the cause of release of DOC upon reductive dissolution of Fe in boreal soils (Hagedorn et al. 2000; Fiedler and Kalbitz 2003; Pan et al. 2016). DOC sorption capacities of Fe oxides in boreal soils range from molar DOC:Fe ratios below 10 (Moore 1988; Hagedorn et al. 2000) to 39 (Musolff et al. 2017). However, while the increase in Fe in the current experiment was in the μmolar range, the increase in

Fig. 5 Mean NO_3^- (a), and PO_4^{3-} concentration (b) in the four treatments over time. *HS* high sulfuric acid treatments, *LS* low sulfuric acid treatments, *O* oxalic treatments, and *A* anoxic treatments. Error bars ± 1 SD. *NF* (white background) and *WF* (grey background) highlight the period before and after the influence of fungal growth in the *O* treatments



DOC was in the *mmolar* range. This suggests that the main explanation behind the higher DOC concentration in the anoxic treatments was not the release of adsorbed/co-precipitated organic carbon from reductive dissolution of Fe, even if it is likely that some OC was released by this process (Skoog and Arias-Esquivel 2009; Pan et al. 2016), but rather that the degradation of DOC was impaired by the lack of oxygen (Bastviken et al. 2004). Finally, given the low Fe:OC ratios in all microcosms ($\sim 5 \times 10^{-4}$), it is not likely that availability of DOC was the main driver behind differences in Fe concentration between treatments. Fe complexing capacities corresponding to Fe:OC ratios between 0.024 and 0.16 for freshwater DOM (Neubauer et al. 2013a; Xiao et al. 2013) suggest that DOC for Fe complexation was available in excess throughout the experiment.

An increase in Fe due to release of Fe(II) in reducing conditions has been previously demonstrated in microcosm experiments (Schuth et al. 2015), and reduction of Fe(III) occurs at higher Eh when soil pH is lowered (Atta et al. 1996). This is further supported by the fact that the increase in total Fe began when the

NO_3^- , a potentially competing electron acceptor, was depleted. The rapid decrease in NO_3^- and increase in PO_4^{3-} , followed by an increase in Fe and Mn, is in agreement with observations by De-Campos et al. (2012) from short-term flooded terrestrial soils. The concurrent increase in PO_4^{3-} with Fe may be due to reductive dissolution of Fe(III) and release of Fe-bound PO_4^{3-} (Ponnamperuma 1972). However, since the increase in PO_4^{3-} far exceeded that of Fe, additional mechanisms such as mineralization of organic matter, or desorption due to lower ionic strength in the microcosms compared to in situ soil conditions (Barrow and Shaw 1979), are required. Our results are in line with previous studies which show that wetting of soils alter redox conditions and result in mobilization of Fe(II) (Ponnamperuma 1972; Knorr and Blodau 2009; De-Campos et al. 2012; Knorr 2013), and that the prevalence of reducing conditions in the catchment control seasonal variability in Fe concentrations in Swedish rivers (Ekstrom et al. 2016).

Fe mobilization from soil to water—the role of S

Contrary to our hypothesis, we found that Fe mobilization was higher in treatments with high SO_4^{2-} concentrations. The positive effect of HS on Fe concentrations may have been caused by the lower pH, enhancing Fe dissolution, as well as Fe solubility (Lindsay 1979). Also Mn concentrations were higher in HS throughout the experiment, further supporting that the lower pH in the high SO_4^{2-} treatments increased solubility and favored reducing activities in anoxic treatments.

There was no loss of SO_4^{2-} , as an indication of sulfide production, over the course of the experiment, but rather an increase, which was probably the result of mineralization of organic material. It is unlikely that SO_4^{2-} reduction occurred in the anoxic treatments since redox never reached below 200 mV in our microcosms, while SO_4^{2-} reduction typically occurs below 100 mV at pH 3–4 (Takeno 2005). The low pH in our experiment, which is typical for organic horizons of boreal soils, may have disfavored SO_4^{2-} reduction since SO_4^{2-} reducing bacteria are sensitive to low pH (Simek et al. 2014), while Fe(III) reducing bacteria cope well at low pH (Blodau 2006).

High S deposition has been suggested to have a negative effect on surface water Fe concentrations by reducing DOC mobility (Neal et al. 2008). Organic complexes enhance the solubility of Fe, and may for instance explain the presence of Fe(II) even in oxic pH-neutral waters (Karlsson and Persson 2012; Daugherty et al. 2017). Affinity of DOC for Fe is reduced at lower pH, due to increased protonation of functional groups of the organic matter (Fang et al. 2015; Neubauer et al. 2013a, b), but Fe can form stable soluble complexes with DOC also in the acidic pH range (3–4) (da Silva et al. 1998). In this study, DOC concentrations were indeed reduced in response to HS, while Fe showed the opposite response. This, and that DOC was available in excess in relation to Fe in all treatments and throughout the experiment, suggest that an indirect effect of HS on Fe via DOC was not a major factor controlling Fe mobilization.

Fungi-induced mobilization of Fe and DOC

A marked increase in Fe concentration in the oxic treatments coincided with detection of fungi dominated by the species *Jaapia ochroleuca* (Bres.) Nannf.

& J. Erikss. *J. ochroleuca* is a rare, but geographically widespread lignicolous species (Eriksson and Ryvar-den 1976), that has been frequently reported on sodden and well-decayed wood of both conifers and hardwoods in Sweden and elsewhere (Nannfeldt and Eriksson 1953; Telleria et al. 2015). Although not studied, the increase in Fe may have been due to solubilization of Fe and associated nutrients for uptake, organic matter decomposition providing labile organic acids for Fe reduction, or due to a Fenton-mediated active system during growth of *J. ochroleuca* (see supplementary material for more information). Fungi employ mechanisms for the solubilization and uptake of Fe found in organic substrates or minerals, including secretion of siderophores with strong affinity to Fe(III) (Landeweert et al. 2001; Kosman 2013; Sørensen et al. 2014) and small metal solubilizing organic acids (Clarholm et al. 2015). Furthermore, generation of Fe(II) for non-enzymatic decomposition of plant cell walls is known to exist in brown-rot fungi (Zhu et al. 2016), and some of those mechanisms may be active in certain ectomycorrhizal fungi as well (Shah et al. 2015). Secretion of reducing agents of Fe(III) (Arantes et al. 2009) facilitate the generation of Fenton reactions, given that a source of hydrogen peroxide exists. As Fenton reactions are most effective at pH < 4 (Zhu et al. 2016), the steep increase in total Fe may have been caused by Fenton reactions induced by the fungus. Although some Fe may have been mobilized by reductive dissolution in the suboxic environment, caused by fungal oxygen consumption, this cannot be the sole explanation considering that Fe concentrations in the oxic treatments exceeded those in anoxic treatments. Regardless of the specific mechanism causing the Fe mobilization, the results demonstrate that the action of fungi can have a significant impact on the release of Fe, and subsequently to the amount of Fe released into freshwater systems.

Transition from anoxic to oxic water in the landscape

DOC could play an important role for Fe stability in the riparian zone where Fe is otherwise sensitive to hydrolysis and precipitation at the oxic-anoxic interface. In our re-oxidation experiment, Fe from the anoxic treatments was stable against precipitation when exposed to oxic conditions and remained in

solution. Either the low pH—and/or the high availability of DOC—in the boreal soil used in this study maintained Fe in solution even during well-oxygenated conditions. Hence, our results suggest that Fe would be mobilized at the conditions of the experimental treatments, and that the mobilized Fe may sustain the transition from boreal soils to surface waters.

Re-introduction of air in another soil incubation experiment resulted in Fe oxide precipitation within 2 days (Schuth et al. 2015). However, pH was higher (> 5) and organic carbon concentrations lower (Schuth et al. 2015) than in the current experiment. Fe(II) oxidation rates are highly sensitive to pH, with Fe(II) dominating around pH 4, and the presence of complexing agents such as OM has been shown to retard oxidation rates (Theis and Singer 1974; Sung and Morgan 1980; Morgan and Lahav 2007; Jones et al. 2014). Fe has been shown to be mainly associated to OM at native pH (~ 4) in podzol extracts, and to precipitate as Fe (oxy)hydroxides as pH increases (Neubauer et al. 2013a, b). Furthermore, previous studies have shown that Fe is enriched in riparian soil waters—mainly as organic Fe complexes (Sundman et al. 2014)—and that Fe and OM to a large extent are exported from this zone to adjacent stream water (Lidman et al. 2017).

Importantly, we studied mobilization of Fe and DOC from the organic soil horizon only, potentially representative of superficial runoff or waterlogging of boreal soils or riparian zones. It is apparent that biogeochemical processes in flooded soils differ depending on land-use (De-Campos et al. 2012), as well as between soil horizons. However, the organic soil layer has been identified as a significant source of Fe compared to deeper soil horizons (Giesler et al. 2000; Lidman et al. 2017). Furthermore, increased precipitation, as has been predicted in climate change scenarios for northern latitudes, has been suggested to lead to dominant flow through superficial soil horizons and an increased leaching of organic compounds (Hagedorn et al. 2000; Hongve et al. 2004; Haaland et al. 2010), and reasonably of DOC associated Fe. Moreover, soil slurries may not be entirely representative of processes in intact soils, where micro-heterogeneity with differences redox conditions, and active vegetation are likely to have an influence (Knorr and Blodau 2009). Somewhat reassuringly, Fe and DOC concentrations in the oxic treatments at the

beginning of the experiment were in the same range as in a field experiment conducted at the same site and with the same SO_4^{2-} treatments (Mean (SD): $\text{Fe}_{\text{LS}} = 4.9$ (4.3) $\mu\text{mol L}^{-1}$, $\text{Fe}_{\text{HS}} = 4.1$ (3.7) $\mu\text{mol L}^{-1}$, $\text{DOC}_{\text{LS}} = 5.8$ (3.5) mmol L^{-1} , $\text{DOC}_{\text{HS}} = 3.9$ (2.9) mmol L^{-1} , pers. communication) (Ekstrom et al. 2011). Hence, while we acknowledge the inherent limitations of soil slurries, we believe these experiments provide important information of Fe mobilization processes in boreal soils.

Conclusions

Since Fe release from the soil was higher in the high SO_4^{2-} treatment, results from this study does not support that reduced atmospheric S deposition is a driver behind increasing Fe concentrations in surface waters. On the contrary, the lower pH as a result of HS likely promoted Fe solubility and Fe(III) reduction, and hence mobilized more soluble Fe species. Although the high availability of DOC for complexation most likely maintained Fe in solution, the fact that DOC was negatively affected by higher SO_4^{2-} concentrations suggests that redox and pH along with mobilizing processes induced by the fungus *J. ochroleuca* were more important in controlling Fe release from soil to the aqueous phase. Hence, although Fe and DOC have been shown to be tightly connected in soils and water, the factors that control their mobilization and concentration in the aqueous phase are partly different. Finally, while Fe is often assumed to be lost in the transition from anoxic to oxic water in the riparian zone, our study show that Fe may stay in solution as anoxic soil horizons connect with oxidized surface water.

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