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Subsurface Fe (II) affects concentrations of dissolved O_2 in streamwater

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ABSTRACT

The interface between groundwater and surface water is a critical zone influencing ecohydrological and biogeochemical cycles within surface water ecosystems. It is characterized by complex redox gradients, with groundwater-mediated inflow of reduced substances affecting the oxygen budget of stream water. In this study, we have experimentally simulated the inflow of Fe(II)-rich groundwater into the open stream water of a flume system to quantify its effect on dissolved oxygen concentration in both the stream water and the hyporheic zone. The experimental setup consisted of 12 flumes, half used for input of groundwater augmented with Fe(II), while the other half served as a control. We studied the effects of coarse (6% fine sediment content) sediment vs. fine (28 % fine sediment content) sediment as well as and moderate (3 L s^{-1}) vs. low (0.5 L s-1) flow rate in a fully-crossed, 3-way-replicated design. Weekly sampling campaigns were performed to analyze Fe(II), Fe(III), DOC, and dissolved oxygen (DO) concentrations in the pore water (hyporheic zone) and in the open water over five consecutive weeks. Our results indicate that Fe(II) inflow substantially decreased DO concentrations in both the pore and open waters. Oxygen uptake rates increased from 7.4 up to 8.6 g O_2 m^{-2} d^{-1} at a moderate flow rate and from 1.7 to 1.9 g O_2 m^{-2} d^{-1} at a low flow rate. This corresponds to a contribution of the Fe(II) input to the overall oxygen uptake rate in the flumes of 21 and 17%, respectively. Treatment with $FeCl_2$ also led to a substantial increase in DOC from $\sim$ 55 mg L^{-1} in the control flumes to $>$ 60 mg L^{-1} suggesting a linkage between Fe(II) mobilization and the occurrence of DOC. In conclusion, this study highlights the need to consider the effects of hyporheic and riparian redox processes and subsequent inflow of Fe(II) into streams on the oxygen budget and the health of stream ecosystems.

1. Introduction

Dissolved oxygen (DO) is one of the most critical parameters of the ecosystemic status in stream water and is required for all lifeforms higher than bacteria (Piatka et al., 2021). Therefore, a sufficient supply of DO is a key requirement for a healthy freshwater ecosystem. DO is of particular importance in those habitats that serve as breeding grounds for fish and a wide range of invertebrates, such as in the hyporheic zone (HZ). For instance, egg-hatching success in salmonid fishes (Smialek et al., 2021; Sternecker et al., 2014, 2013; Wild et al., 2023) as well as recruitment in endangered invertebrate species such as the freshwater pearl mussel (*Margaritifera margaritifera*) have been linked with substrate properties of the stream bed governing oxygen supply (Denic and Geist, 2015; Geist and Auerswald, 2007; Hoess and Geist, 2020). Consequently, DO availability shapes habitat quality and, thus, biological community structures.

Stream oxygen concentrations typically reflect a balance between O_2 production via photosynthesis (i.e. primary production) and ecosystem respiration consuming DO (ER) (del Giorgio and Williams, 2005; Demars et al., 2015; Kosten et al., 2014; Piatka et al., 2021; Solomon et al., 2013). Oxygenic metabolism is generally the dominant pathway of ecosystem respiration (Raven, 2009), but gross respiration estimates will also include anaerobic metabolic pathways via oxidation of respiration products transferred into the stream and hyporheic water by advective/diffusive processes (del Giorgio and Williams, 2005; Trimmer et al., 2009). Hence, ER accounts for a series of oxidation reactions such as nitrification (Hall and Jeffries, 1984) including photooxidation of organic matter (Estapa et al., 2012).

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Surprisingly, ferrous iron (Fe(II)) has hardly been discussed as a candidate to contribute to ER, albeit there is increasing evidence for Fe (II) to enter streams under gaining conditions when reduced groundwater comes into contact with the HZ and the stream water itself (Benner et al., 1995; Berube et al., 2018; Dong et al., 2020; Kwak et al., 2024). Consideration of the role of subsurface Fe(II) fluxes for the stream water oxygen budget attains even more important against the background that widespread increases in iron concentration in European and North American freshwaters have been observed (Björnerås et al., 2017). While control of groundwater-driven input of Fe as well as maintenance of well-defined stream conditions is difficult to obtain in the wild, a unique flume setup mimicking natural stream systems at the Aquatic Systems Biology Unit at TUM (Wild et al., 2023) enabled us to run a controlled experiment on the role of subsurface Fe(ii) introductions for the DO budget of streams.

In this work, we studied the role of subsurface (pore-water) Fe(II) for the DO budget of streams and their hyporheic zone. We hypothesized that Fe(II) oxidation substantially affects the DO budget in both surface and subsurface water. To this end, we have experimentally simulated the inflow of Fe(II)-rich subsurface water in the stream water using a stream-like flume system and quantified its effect on stream and pore-water DO concentrations at different flow rates and sediment composition.

2. Materials and methods

2.1. Experimental design

The experiments were performed in a flume system, allowing us to experimentally study the role of sediment composition and flow rate in surface-water quality as affected by subsurface Fe(II) flow to the flumes. The flume system was constructed as an outdoor experimental flume mesocosm facility located in the direct vicinity of the River Moosach at the Aquatic Systems Biology Unit of Technical University of Munich in Freising, Germany and is supplied with groundwater that is available on-site through a combined pumping and storage system.

Sediments consisted of the same sediment mixtures, however with a variable proportion of fine sediment (Wild et al., 2023). While in the coarse sediment treatment, the average proportion of fine sediment (<0.85 mm) was 6 ± 0.3 %, the proportion of fine sediment was increased to 28 ± 2.9 % in the fine sediment treatment. The saturated hydraulic conductivities of the two materials were estimated to be 0.01 m s^{-1} for the coarse material and 0.0002 m s^{-1} for the fine material (Beyer, 1964)

Surface-water flow is separated from subsurface flow by a sediment layer, establishing a vertical subsurface flow component. The system is composed of 12 flumes that were further subdivided into two separate

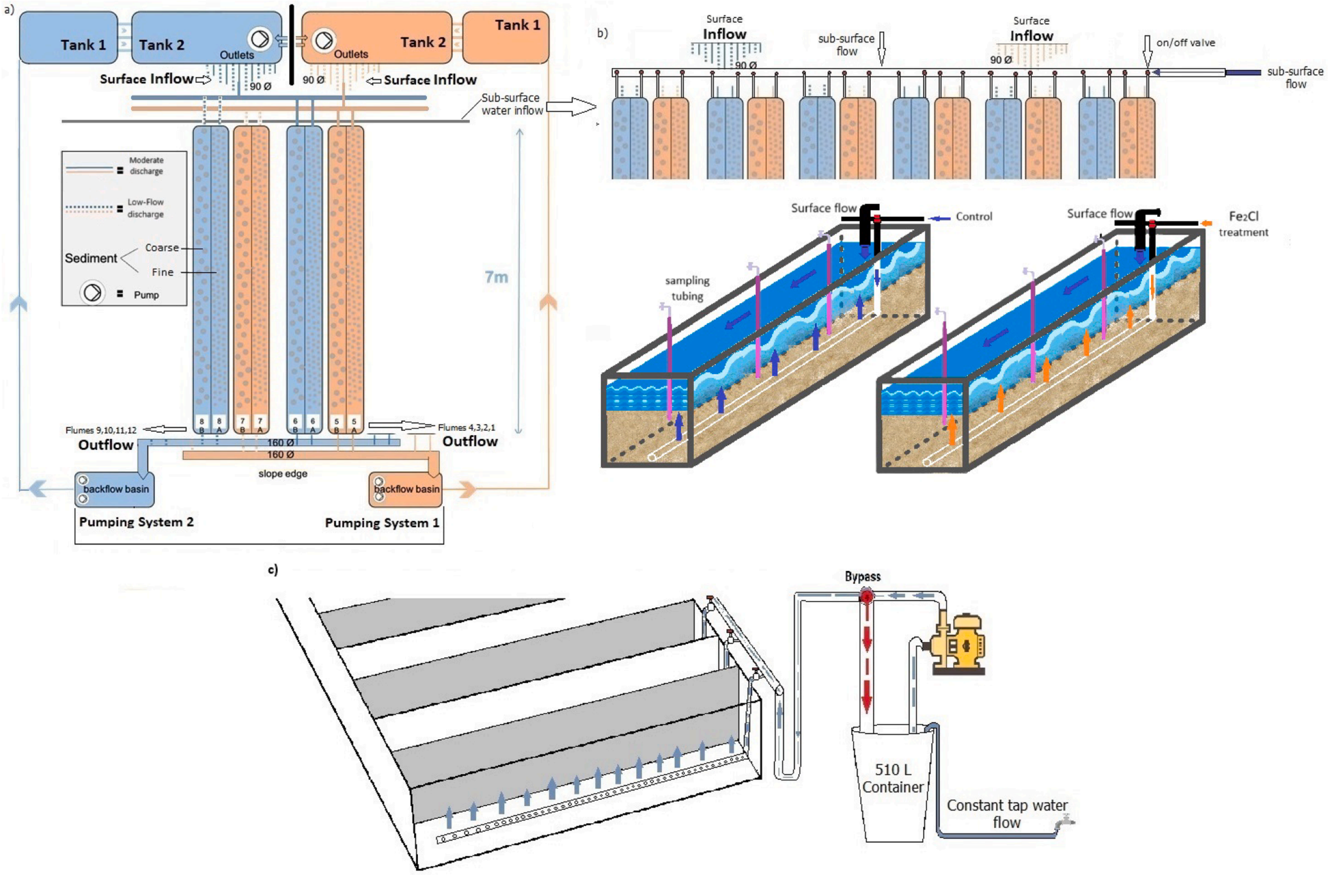

Fig. 1. a) Scheme of the flume system used in this experiment, exemplified for flumes 5–8. Each flume was separated into sub-flumes A and B. All sub-flumes A were filled up with fine sediments, and all sub-flumes B were filled up with coarse sediments. Six flumes were exposed to moderate (3 L s^{-1}) discharge (continuous line at the inlet to flumes 5 and 6), and 6 flumes simulating discharge under low-flow (6 L s^{-1}) conditions (dotted lines at the inlet to flumes 7 and 8). Flumes with uneven numbers (in orange, flume numbers 1–11) supplied with the pumping system 1 were treated with $FeCl_2$. Flumes with even numbers (in blue, flume numbers 2–12) were the control flumes, supplied through pumping system 2. After passing through the flumes, the water flowed to two collection tanks from where it was pumped back into the respective upper collection tanks for storage. b) Scheme of the subsurface flow into the flume. The subsurface units in the flume cells are supported by a separate water supply which is independent from the surface discharge. The cross-section plot illustrates the Fe (II) supply into a treated flume and the supply of Fe (II)–free water in a control flume. The sampling tubing was installed at three different positions along the flume. c) Scheme of the water supply system for subsurface flow. Tap water is constantly circulated in a container disclosed from the atmosphere (with the opportunity of replacement of water from the tap). The bypass regulator allowed for a steady flow of 0.25 L min^{-1} into the subsurface compartments of one single flume cell.

units per flume by an internal vertical divider (Fig. 1a), allowing for running 24 experiments in parallel. The 24 flumes allowed a fully replicated design to study individual and combined stressor effects with three replicates (individual flumes) within each treatment. The identical setup with some experimental modifications had previously been proven successful in testing the effects of fine sediments, flow, and temperature on the recruitment (survival and growth) success of freshwater fishes (Wild et al., 2023). To study the influence of subsurface inflow through iron-rich sediments on DO concentrations in the surface water and sediment porewater, we injected a Fe(II) containing solution into the sediment of twelve of the flumes (Fig. 1a and b). The remaining 12 flumes were established as experiment controls (blue color in Fig. 1). After 2 h of equilibration, constant levels of solute concentrations were established. The sediment composition (fine vs. coarse) and surface flow rate (low (0.5 L s^{-1}) vs. moderate (3 L s^{-1}) differed between the flumes, yielding 4 variants with 3 replicates for both the Fe(II) treated and untreated flumes. The experimental setup is described in detail in the Supporting Information (Supplementary Note: Experimental Setup).

2.2. Filling protocol of the FeCl2 treatment flumes

Filling the flumes with a $FeCl_2$ solution was achieved using the subsurface pumping system described above. We targeted a complete filling of the pore waters of a single flume with a solution containing an initial concentration of 0.1 mmol L^{-1} Fe(II) as $FeCl_2$. The dilute $FeCl_2$ solution was prepared from a liquid $FeCl_2$ flocculation reagent (KEMIRA PIX-209, Germany) mixed with chlorine-free tap water. The tap water was purged with nitrogen, a residual DO concentration of 3–4 mg L^{-1} could not be avoided though. For the calculation of the volume of diluted $FeCl_2$ required to fill the subsurface volume of the flumes, we assumed a porosity of 0.3 for both sediment types, A (fine) and B (coarse). The pore volume for one flume cell (A or B) is 525 L, so 1050 L of diluted $FeCl_2$ was filled into the $FeCl_2$ treatment flumes simultaneously at a filling velocity of 75 L per minute (Fig. 1c). During the $FeCl_2$ filling procedure in the treatment flumes, the surface water flow of these flumes (PS1) was reduced to the minimum to keep oxygen penetration at a minimum.

Each flume cell was gently filled with $FeCl_2$ solution diluted in water using three containers (350 L) from which the solution was pumped via the subsurface water entrance port into the corresponding flume (Fig. 1c). The containers were purged with N_2 prior to filling. During the filling of each sub-flume, the total Fe concentration was checked in the first container to be used, and a range of 0. 1mmol L^{-1} Fe (II) ± 0,01 mmol L^{-1} was determined. The pH of the diluted solution ranged between 6.5 and 7.5. Filling of the flumes was performed within one day, and the experiments were started at the following day.

2.3. Sampling protocol

Sampling was performed over five weeks starting on October 15, 2021, after adding $FeCl_2$. Polyurethane sampling tubes (4.2mm internal diameter size, Fig. 2c) with a filter fabric at the bottom end and a high flow Stopcock 4-way syringe valve at the top end were installed at 3 points in the flume, at the inflow, the center, and the outflow of each flume cell at a depth of 10 cm.

Immediately after filling, samples were taken from the surface and subsurface waters in the FeCl2-treated flume cells. The samples were collected with individual syringes and transferred to sampling vials. All samples were filtered through 0.45 μm pore size filters. In order to preserve the redox speciation of dissolved iron, a subsample was added into 15ml vials containing 100 μL of 1 molar HCl. In total, we collected six samples of surface and pore water for each flume which is one sample per cross section (inflow – center – outflow location).

In order to minimize oxygen concentration disturbances, we performed the measurements of the oxygen concentration in the pore waters in a flow-through glass 20 ml cell. In this cell, DO concentrations were determined using an optic contactless oxygen microsensor dot with optical isolation (Self-Adhesive Trace Range Oxygen Sensor spots TROXSP5-ADH, Pyroscience, Aachen, Germany) pasted to the outside of the glass cell. We used an optical fiber cable (Optical Fiber with lens

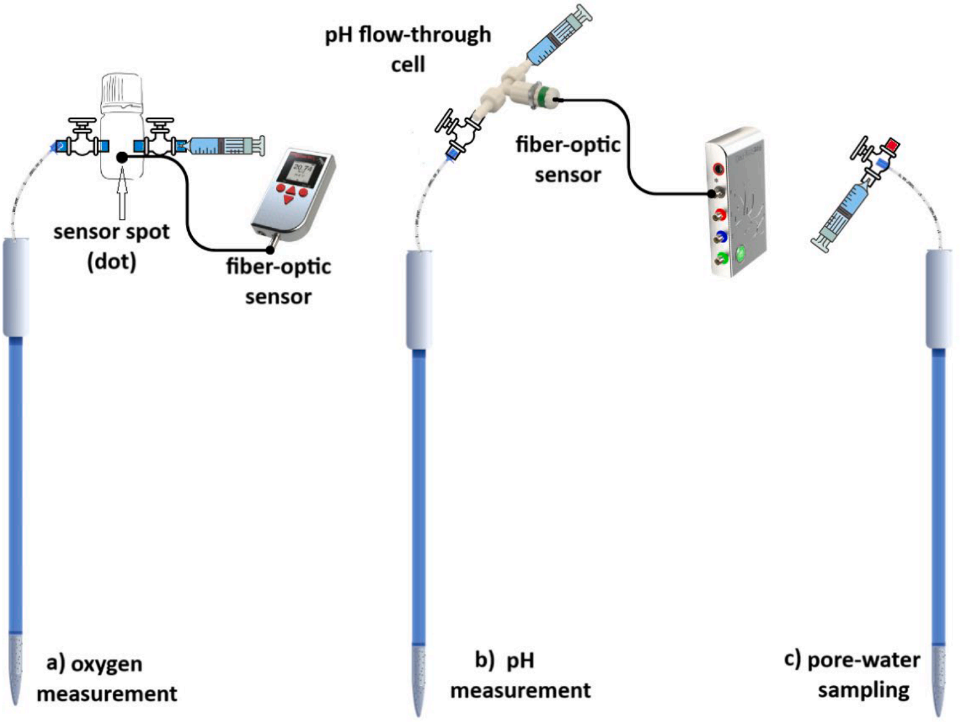

Fig. 2. Sub-surface water sampling and measurements. a) oxygen measurement system with an optic sensor dot, b) pH measurement system with a flow-through cell, c) sub-surface water sampling system.

SPFIB_LNS, diameter 3mm, length 1m of bare polished fiber tip of 2mm and ca. 8mm length, Pyroscience, Aachen, Germany) attached to an optical dot through the optical insolation device for measurement. The readouts were taken with a pocket oxygen meter (FireSting-GO$_2$, Pyroscience, Aachen, Germany). The glass cell had 2 valves installed on opposite sides. The inlet valve was connected to the valve of the sampling tube, and the outlet valve to a sterilized syringe. The pore water was directly filled into the glass cell by suction until no gas phase was left (Fig. 2b). Prior to filling, the glass cell was purged with N$_{2.}$ The glass cell was hermetically closed in the top part. For surface-water samples, the same setup was used.

The pH values were determined using a pH flow-through cell with an integrated pH sensitive luminescent indicator and an optical fiber sensor readout (PFIB-BARE Optical fiber core Ø = 1mm, Ca. 1m length, PyroScience GmbH Aachen, Germany). (Fig. 2a). Two different sensors were used depending on the pH range (PHFLOW-PK5 in the pH range between 4 and 6 and PHFLOW-PK7 in the pH range between 6 and 8, PyroScience GmbH Aachen, Germany). At both ends of the cell, a valve was connected. The first valve was connected directly to the sampling tube, and the other to a sterilized syringe that pulled the sample through the cell. Calibration of the pH sensors was performed at pH 2 and pH 11 using calibration capsules provided by the manufacturer (PHCAL2 and PHCAL11, PyroScience GmbH Aachen, Germany). The readout was made using the optical pH Temp Meter FireSting®-PRO.

2.4. *Analytical methods*

Fe(II) and total iron (Fe$_{\mathrm{Tot}}$) were determined photometrically in both filtrated and unfiltrated samples in a two-step process using the phenanthroline method (Tamura et al.,1976). First, Fe(II) was determined after the addition of 2 mL of sample and 500 µL phenanthroline solution (0.5%) to a cuvette containing 500 µL of an acetate buffer (pH4.5). Then, after measurement of the absorbance, 200 µL of ascorbic acid (10%) was added to the first mixture and allowed to rest for 30 min to reduce Fe(III) to Fe(II) before measuring the absorbance of the sample at 512nm. DOC/DIC analysis was carried out with a TOC-L-Analyzer (Shimadzu).

2.5. *Statistical analysis*

Statistical data analysis was performed using the R statistical package "rstatix" (Pipe-Friendly Framework for Basic Statistical Tests). The package contains helper functions (“identify outliers”, “Mahalanobis distance”, “Levene’s Test”, and “Shapiro-Wilk Normality Test”) for identifying univariate and multivariate outliers and assessing normality and homogeneity of variances. Statistical comparison between treatments was carried out with the non-parametric Kruskal-Wallis test to account for the non-normal distribution of in-flume measurements, followed by the non-parametric Dunn’s test to identify which groups are different. The null hypothesis tested was that the two samples had the same median concentrations of oxygen. The null hypothesis was rejected for $p < 0.05$.

3. Results

3.1. *Temporal development of the hydrogeochemistry in the flumes*

Treatment of the flume sediments with FeCl$_2$ substantially perturbed the biogeochemical patterns in the flume cell. Along with the addition of Fe(II), a substantial drop in pH occurred with pH < 4 in the pore water and < 5 in the surface water (Fig. 3), irrespective of the variants (see Supplementary Fig. SI1 online). Such pH drop can be attributed to the oxidation of Fe^{2+} to Fe^{3+} by residual oxygen in the subsurface water and the subsequent hydrolysis of Fe^{3+} to form a ferric oxyhydroxide (FeOOH,Stumm and Morgan, 1996).

$$\mathrm{Fe^{2+} + ¼\ O_2 + 1.5\ H_2O \rightarrow FeOOH + 2\ H^+} \tag{1}$$

The pH increased again after two weeks and reached a constant level of slightly above 5 in the pore waters and above 6 in the surface waters. In the control group, the pH remained close to 8 in the surface waters and around 7 in the pore waters. The initial drop in pH in the treated flumes was accompanied by high concentrations of dissolved Fe(II) (~ 50 µmol L^{-1}) in the pore waters and ~ 20 µmol L^{-1} in the surface waters (see Supplementary Fig. SI2 online), while in the control flumes, the concentrations of dissolved Fe(II) ranged between 0.4 and 12.8 µmol L^{-1} for both surface and porewater.

Along with the increase in pH after 2 weeks, the Fe(II) concentration in the pore water decreased continuously to values around ~ 20 umol L^{-1}. Such values are typically found in many shallow groundwaters (Eckerrot and Pettersson, 1993; Samarina et al., 2020). The occurrence of dissolved Fe(II) was accompanied by the appearance of filterable Fe (III) with particularly high concentrations (~20 µmol L^{-1}) at the beginning of the experiment. In contrast, Fe(II) concentrations in the control experiments remained very low (see Supplementary Fig. SI2 online).

The addition of Fe(II) substantially impacted the concentrations of dissolved oxygen (DO, Fig. 4). In particular, pore-water DO concentrations in the treated flume cells were significantly ($p < 0.05$) lower compared to the control, irrespective of the initial drop in pH, with values as low as 6 mg L^{-1}. It appears that the occurrence of Fe(II) in the pore waters even affected mean DO surface water concentrations, which were significantly lower ($p < 0.05$) in the treated flumes (mean value 8.4 mg L^{-1}) than those in the control flumes (9.1 mg L^{-1}, see Supplementary Fig. SI3a online).

Interestingly, the DOC concentration in the surface and porewater was also affected by the treatment with FeCl$_2$. DOC concentrations were generally high in the control experiments (55 mg/L on average, Fig. 5). Treatment with FeCl$_2$ led to fluctuations between 31 and 67 mg L^{-1} in DOC concentrations in the first two weeks. DOC concentrations in the final phase of the experiment (weeks 3 – 6) were significantly higher than in the control flumes with values > 60 mg (Fig. 4), irrespective of the experimental variant (see Supplementary Fig. SI4 online).

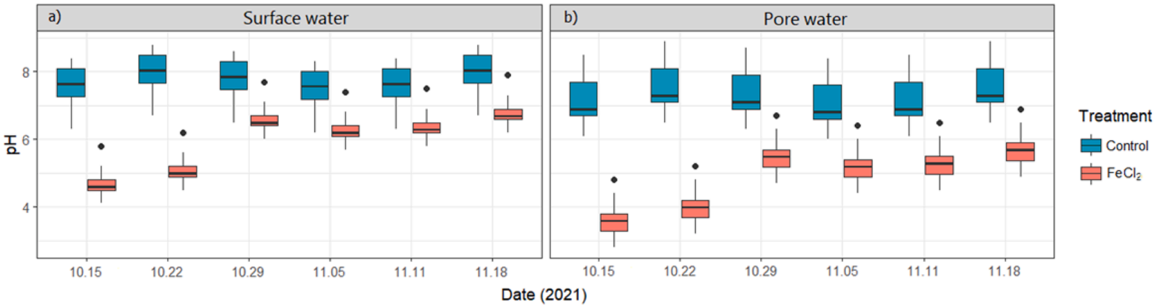

Fig. 3. The pH values shift between control and treated flumes in the a) surface and b) porewaters.

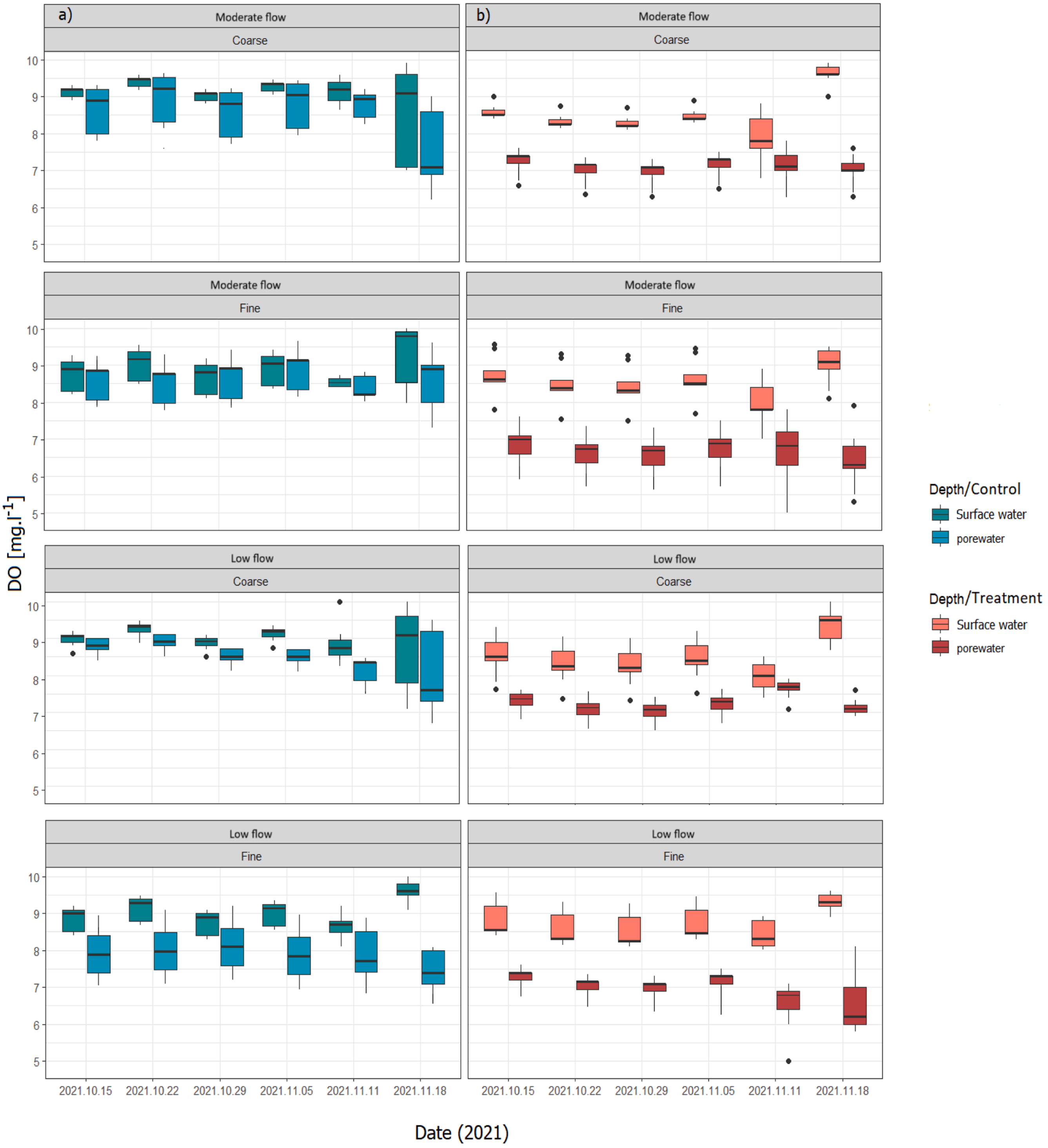

Fig. 4. Temporal trend of DO between a) control flumes and b) treated flumes.

3.2. *Effect of flume parameters on DO concentrations in the flumes*

The flume parameters substantially affected the impact of $FeCl_2$ addition on dissolved oxygen concentrations (see Supplementary Fig. SI5 online). For statistical analysis, we used values only from the last four weeks of the experiments, after which constant pH values had been established. A significant difference in pore-water DO concentration between coarse and fine sediment could be observed in treated and untreated flume cells (see Supplementary Fig. SI5 online), with higher values in coarse sediments. Mean values were 8.9 and 7.7 mg L^{-1} in the control flumes for the coarse and fine sediment, respectively, and 7.2 and 6.8 mg L^{-1} in the $FeCl_2$ treatment flumes, respectively. In contrast, DO concentrations in surface waters did not show a dependence on flume parameters. Flow rates did not affect DO concentrations in surface waters, irrespective of the sediment composition (see Supplementary Fig. SI5a online). Also, in pore waters, flow rates seem to play a minor role in the control of DO concentrations (see Supplementary Fig. SI5b online), with a tendency to slightly higher values at the moderate flow rate in flumes with reference discharge. Overall, DO concentrations in pore waters were substantially influenced by sediment grain size

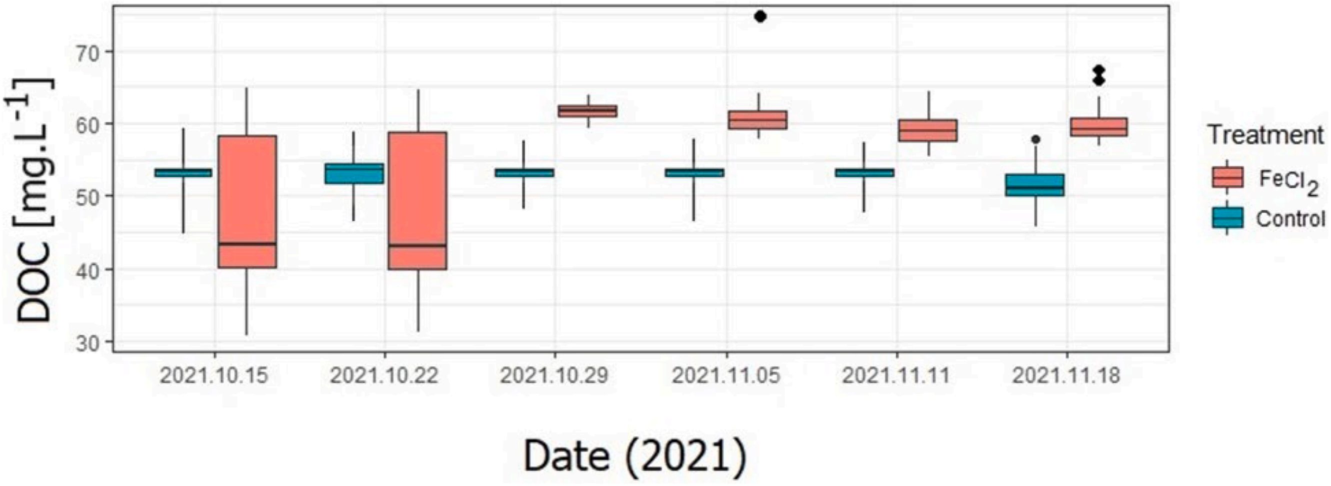

Fig. 5. DOC concentrations in all samples (pore and surface waters) from controls and treated flumes.

(Fig. SI5b); the effect was strongly amplified in the treated flume cells.

4. Discussion

4.1. Effect of pore water Fe(II) on stream oxygen uptake rates

Our results clearly demonstrate that Fe(II) supply from the subsurface can have a substantial effect on the oxygen budget of streams, particularly within their hyporheic zone, which provides an important habitat for many species (Boulton et al., 1998; Geist, 2010; Greig et al., 2007; Nagel et al., 2020). The results show that the advective supply of Fe(II) reduces pore water and stream DO concentrations relative to the control. The effect is larger in stream beds of lower porosity.

In order to quantify these effects, we have compared the overall oxygen uptake of the streambeds in the control experiments with that of treated cells by use of a steady-state mass balance approach (Demars et al., 2015) with the oxygen concentration in the controls as the reference state:

$$\frac{dc(O_2)}{dt} = k_{O_2}\ .\ \left(c(O_2)_{sat} - c(O_2)_{flume}\right) + GPP - UR \qquad (2)$$

With,

$c(O_2)_{sat}$: Calculated oxygen concentration at saturation at the measured flume temperature, which was 11.3 g m^{-3} (T = 12°C) as derived from Henry's law.
$c(O_2)_{flume}$: mean oxygen concentration measured in surface water of the flumes treatments or the control cells [g m^{-3}],(Table 1)
$k_{O2:}$ Oxygen transfer coefficient [d^{-1}]
GPP: gross primary production rate [g O_2 m^{-3} d^{-1}]
UR: Flume O_2 uptake rate [g O_2 m^{-3} d^{-1}]

The GPP rate at the time of the experiment (November) can be assumed to be negligible and was set to zero. With this the flume-cell O_2 uptake rate accounts for all processes that consume dissolved $O_{2,}$ i.e., respiration but also oxidation of Fe(II). The oxygen transfer coefficient k_{O2} (d^{-1}) accounts for the rate at which O_2 is transferred between the air and surface water, and which largely depends on mean flume-flow velocity and mean flume depth. Values for k_{O2} were calculated by use of two empirical equations formulated from re-aeration experiments by O'connor and Dobbins (1958, Eq. (3)) and Negulescu and Rojanski (1969, Eq. (4)).(Negulescu and Rojanski, 1969; O'connor and Dobbins, 1958)

Table 1
Uptake rates of oxygen in the flume cells with and without Fe(II) addition and the increase in uptake rate induced by the presence of Fe(II).

Flow rate [L s^{-1}]	3		0.5	
Flow velocity [m d^{-1}]	5200		870	
Coarse Sediment				
Control				
Mean c(O_2) [g m^{-3}]	9		8.9	
	eq. (2)	eq. (3)	eq. (2)	eq. (3)
UR [g O_2 m^{-2} d^{-1}]	7.05	1.65	3.00	0.37
Treatment				
Mean c(O_2) [g m^{-3}]	8.6		8.40	
UR [g O_2 m^{-2} d^{-1}]	8.26	1.93	3.62	0.45
Increase in Ur [g O_2 m^{-2} d^{-1}]	1.21	0.28	0.62	0.08
Fine Sediment				
Control				
Mean c(O_2) [g m^{-3}]	8.9		9	
	Eq. (2)	Eq. (3)	Eq. (2)	Eq. (3)
UR [g O_2 m^{-2} d^{-1}]	7.35	1.72	2.88	0.36
Treatment				
Mean c(O_2) [g m^{-3}]	8.6		8.5	
UR [g O_2 m^{-2} d^{-1}]	8.26	1.93	3.50	0.44
Increase in UR [g O_2 m^{-2} d^{-1}]	0.91	0.21	0.62	0.08

$$k_{1,O2} = 3.904\frac{\overline{u}^{0.5}}{\overline{d}^{1.5}} \qquad (3)$$

and

$$k_{2,O2} = 10.92\left(\frac{\overline{v}}{\overline{d}}\right)^{0.85} \qquad (4)$$

with

$\overline{u}$: mean surface flow velocity, which was 5200 m d^{-1} for the moderate and 870 m d^{-1} for the low flume flow rate.
$\overline{d}$: mean flume depth, 0.1 m)

These two expressions provide a range of oxygen transfer coefficients that can be used to further compare oxygen uptake rates with other reports on ecosystem respiration. Assuming steady-state conditions, estimates for area normalized molar oxygen uptake rates UR* in the control and treated flume cells can be calculated as:

$$UR^{*} = k_{i,O2}\ \cdot\overline{d}\cdot\left(c(O_2)_{sat} -\ c(O_2)_{flume}\right) \qquad (5)$$

with units of mg O_2 m^{-2} d^{-1}.

Uptake rates in the control flumes ranged, accounting for both sediment types, between ~ 1.65 g O_2 m^{-2} d^{-1} (Eq. (4)) and ~ 7.35 g O_2 m^{-2} d^{-1} (Eq (3).) for the moderate flow rate and ~ 0.36 g O_2 m^{-2} d^{-1} and ~ 3.0 g O_2 m^{-2} d^{-1} respectively, for the low flow rate (Table 1) which is in the order of rates reported for natural freshwater streams (Demars et al., 2015; Haggerty et al., 2009; Hotchkiss and Hall, 2014; Parkhill and Gulliver, 1998). In the treated flumes, the uptake rates increased to values between ~ 1.93 g O_2 m^{-2} d^{-1} (Eq. (4)) and 8.26 g O_2 m^{-2} d^{-1} (Eq. (3)) at moderate flow rate and between 0.44 g O_2 m^{-2} $d^{-1,}$ and 3.62 g O_2 m^{-2} d^{-1} at low flow rate, respectively. These values correspond to mean increases in uptake rates by between 12 and 17 % in the moderate-flow flume cells and 21 % in the low-flow flume cells implying a substantial effect of subsurface Fe(II) input on the overall DO budget in the flumes.

4.2. Sensitivity of stream ecosystem respiration to Fe(II) fluxes

Fe concentrations in stream waters appear to be on the rise. In a survey on temporal trends of Fe concentrations across 340 water bodies in northern Europe and North America (Björnerås et al., 2017) demonstrated that Fe concentrations have significantly increased in 28% of monitored sites, and decreased in 4%, with the most positive trends located in northern Europe. They conclude that the phenomenon of increasing Fe concentrations is widespread, especially in northern Europe, with potentially significant implications for wider ecosystem biogeochemistry.

In their study, Björnerås et al. (2017) were not able to distinguish between Fe(II) and Fe(III). However, there is evidence that a substantial fraction of the input of iron, particularly from reducing peat riparian soils, is Fe(II) (Blaurock et al., 2022; Curtinrich et al., 2021; Knorr, 2013; Selle et al., 2019). It has been suggested that rising temperatures may even stimulate the mobilization of Fe (Curtinrich et al., 2021) due to an increase in reducing conditions. Thawing permafrost soils appear to seasonally release substantial amounts of Fe(II) into streams (Barker et al., 2023). Input of Fe(II) through drains and ditches in agricultural soils has been observed in wide areas of central European lowlands (Baken et al., 2015; van der Grift et al., 2018). In these studies, the focus was put on the coupling between Fe(II) oxidation, the formation of ferric colloids, and the retention of phosphate (Baken et al., 2013; Smolders et al., 2017; Van Der Grift et al., 2014). Surprisingly, the role of Fe(II) oxidation for the oxygen budget in the streams has not been addressed by now.

In their survey, (Björnerås et al., 2017) emphasized that regions with rising Fe concentrations tend to coincide with those with increases in organic carbon (OC) concentration. Increasing Fe concentrations were paralleled by increasing OC contents in 77% of the waters studied. Organic carbon is well known to stabilize Fe(II) against oxidation via complexation and hinders subsequent precipitation as ferric hydroxides (Daugherty et al., 2017; Theis and Singer, 1974; Zhou et al., 2021) which may also explain the coupled increase both in DOC and in Fe(II) concentrations observed in the flume surface waters of our experiments.

5. Conclusions

Dissolved oxygen supply is a crucial aspect of the health of freshwater ecosystems, especially in habitats such as hyporheic zones that are important for the reproduction of fish and a wide range of invertebrates. DO availability is determined by the dynamic balance between primary production (photosynthesis) and ecosystem respiration (ER) processes, of which the role of ferrous iron (Fe(II)) as a contributor to ER has been underestimated. Our experiments clearly demonstrate that subsurface supply of Fe(II) significantly affects DO concentrations in surface water and hyporheic sediment pore water. Collectively, our results indicate a strong coupling between stream-water DO concentrations, oxygen uptake-rates, and input of Fe(II), which needs to be accounted for in future freshwater ecological studies. Against the background of rising groundwater contribution to discharge during drought-affected low-flow conditions in headwater streams (Kaule and Gilfedder, 2021) these systems may be particularly sensitive to Fe(II) related oxygen uptake.

CRediT authorship contribution statement

Silvia Parra-Suarez: Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Romy Wild:** Project administration, Methodology, Conceptualization. **Benjamin S. Gilfedder:** Methodology, Conceptualization. **Juergen Geist:** Writing – review & editing, Methodology, Conceptualization. **Johannes A.C. Barth:** Writing – review & editing, Conceptualization. **Sven Frei:** Writing – review & editing. **Stefan Peiffer:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Silvia Parra-Suarez reports financial support was provided by Bavarian State Ministry of Science and the Arts. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2025.123368.

Data availability

Data will be made available on request.

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